VOL. XV. 1909

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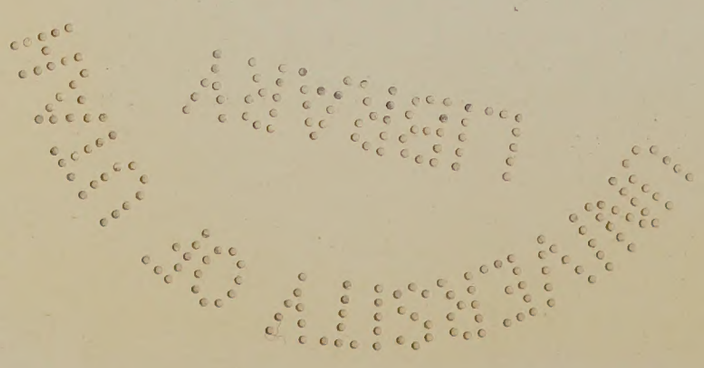

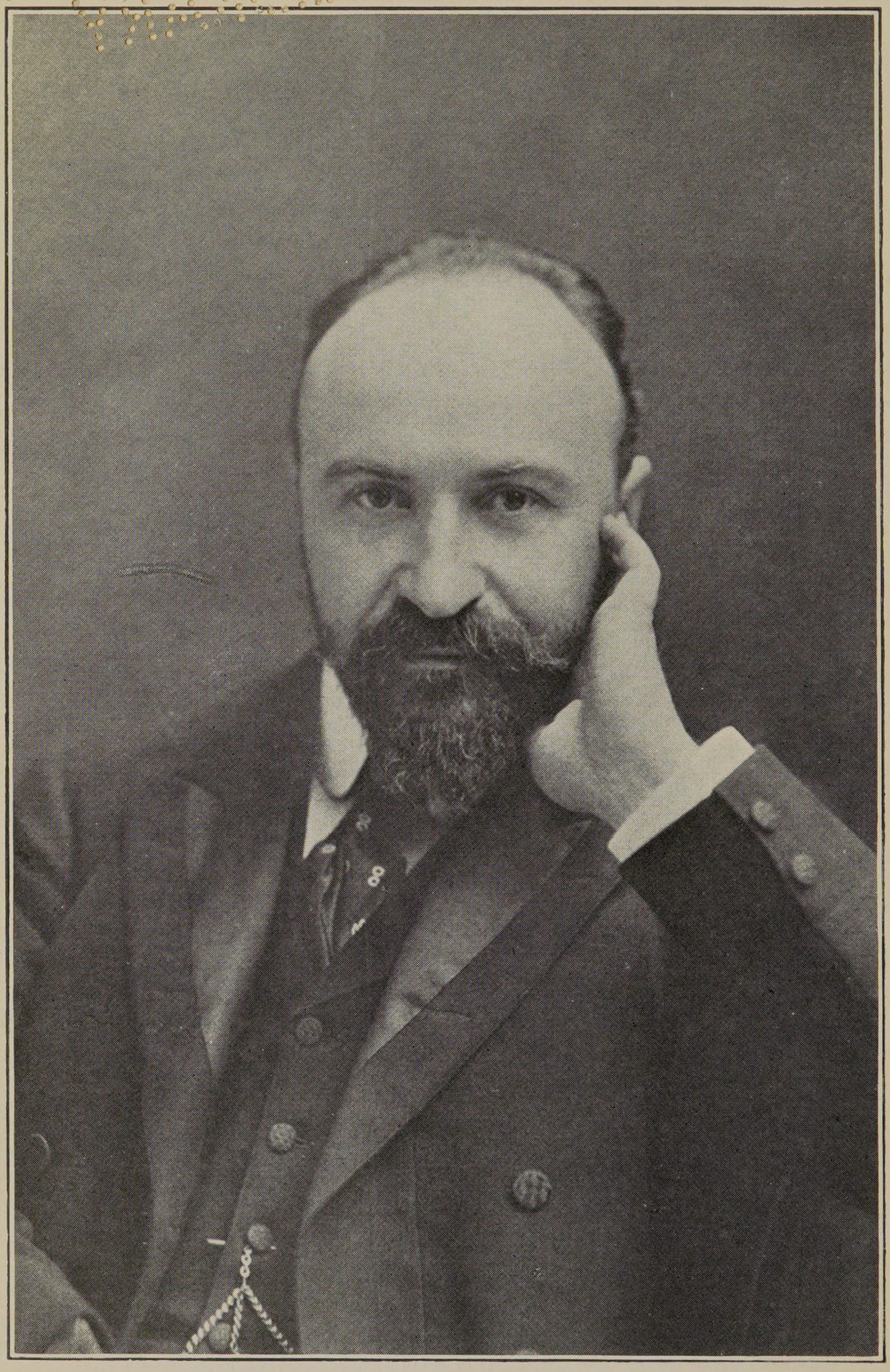

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TRANSACTIONS

OF THE

AMERICAN

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VOLUME XV.

157543

FIFTEENTH GENERAL MEETING

NIAGARA FALLS, CANADA, MAY 6, 7, 8, 1909

PUBLISHED BY

THE AMERICAN ELECTROCHEMICAL SOCIETY

LEHIGH UNIVERSITY, SOUTH BETHLEHEM, PA.

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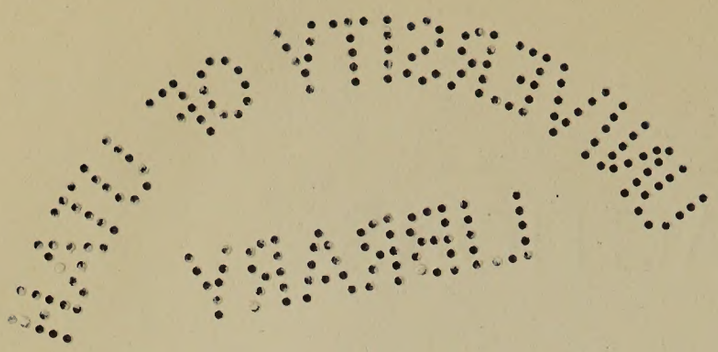

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VOLUME XV. 1909.

TRANSACTIONS

OF THE

AMERICAN ELECTROCHEMICAL SOCIETY

PROCEEDINGS

CONDENSED MINUTES OF THE FIFTEENTH GENERAL MEETING OF THE SOCIETY, HELD AT NIAGARA FALLS, CANADA, MAY 6, 7 and 8, 1909.

Number of members registered, 187; guests, 136; total, 323.

SESSION OF MAY 6th.

The morning meeting was called to order at 9.30 o'clock, in the convention hall of the Clifton Hotel, President E. G. Acheson in the Chair.

President Acheson remarked upon the fact that this was the first meeting of the Society outside the boundaries of the United States, showing the truly international character which the Society is assuming, and introduced Dr. Eugene Haanel, Director of Department of Mines, Canada.

Dr. Haanel welcomed the Society to Canada as follows:

"Mr. President and Gentlemen of the Electrochemical Society:

"It gives me extreme pleasure to welcome you, on behalf of Canada, for your first meeting on Canadian soil. In connection with the subject which I am about to present to you—the examination of a new furnace invented in Sweden for the production of pig iron by the use of electric energy—I desire to

make the statement that we are only on the outskirts of the developments and discoveries of that extremely important branch of electrometallurgy which concerns itself with the extraction of the metals from their ores by the heat resulting from the transformation of electricity. Much has already been accomplished, I admit, but we are only beginning to see our way into the practical application of electricity to the smelting of ores other than those of iron. This subject is of extreme importance to countries like the central provinces of Canada, which lack metallurgical fuel, but possess abundant water-power.

"We look to you, gentlemen of this Society, and to your investigations, to fully open up this storehouse of new processes and to hasten the time when the electric smelting of ores will have replaced the older and well known processes. When I look into the future, it does not seem unlikely to me that a time may come after the richer and more easily treated iron ores have been exhausted and only refractory ores remain, when those magnificent stacks at Pittsburgh and in England will stand as the monuments of a departed process of smelting iron ores." (Applause.)

Papers by Dr. Eugene Haanel, Director of Mines, Canada; P. McN. Bennie; Prof. Dosey A. Lyon; Prof. Jos. W. Richards, on the electric furnace production of pig iron, were communicated and discussed, as printed in full in these Transactions. Papers by Cavalier Ernesto Stassano, of Turin, Italy (read by Jos. W. Richards); Ch. A. Keller, of Livet, France (read by P. McN. Bennie); Paul Girod, of Ugine, Savoy (read by L. E. Saunders, supplement by Jos. W. Richards); Robert Turnbull (read by F. A. J. FitzGerald; and Gustave Gin (read by F. A. Lidbury), on electric furnace manufacture of steel, were communicated and discussed, as printed in full in these Transactions, Dr. J. A. Mathews, of Syracuse, N. Y., opening the general discussion.

The afternoon meeting was called to order at 2.45 o'clock, at the same place, President E. G. Acheson in the Chair.

Mr. Louis Simpson, of Ottawa, Canada, was introduced by the Chair, and on behalf of the owners of water-powers in Canada advised that serious attention be given the question of the electrometallurgy of iron and steel in Canada. His remarks in full will be found in the discussions, as printed in these Trans-

actions. Papers by Gustave Gin (read by Jos. W. Richards); Gustave Gin (read by Carl Hering); A. Kjellin (read by John Hay, of London, England); Carl Hering; F. A. J. FitzGerald; Gustave Gin (read by F. A. Lidbury); Remo Catani, of Elba, Italy (read by Jos. W. Richards); and Henry D. Hibbard, on electric induction furnace manufacture of steel and the properties of electric steel, were communicated and discussed, as printed in full in these Transactions, the discussion being opened by A. Victorin, of New York City.

Papers by Chas. E. Foster and C. A. Hansen were then communicated, the discussion of the last paper being postponed to the session of Friday morning.

The evening session convened at 8 o'clock, when President E. G. Acheson delivered his presidential address up the subject: "The Electrochemist and the Conservation of Our Natural Resources."

A "smoker" was inaugurated at 9 o'clock, terminating with an entertaining session of "Section Q," which was greatly enjoyed by everyone, even by those "hit" the hardest.

SESSION OF MAY 7th.

The Board of Directors met at 9.30 A. M., and held an adjourned meeting at 5.30 P. M.

BUSINESS MEETING OF THE SOCIETY.

The Society convened at 10.30 A. M., President Acheson in the Chair.

The reading of the minutes of the Fourteenth General Meeting was dispensed with, and they were approved as published in the Transactions, Volume XIV.

The report of the Board of Directors, including those of the Secretary and of the Treasurer, was read by the Secretary and accepted for publication in the proceedings of the meeting, to which it is herewith appended. (Mr. Carl Hering called attention to the anomaly, that the expenses of running the Society and printing and distributing its Transactions were nearly $6.50 per year per member, which was being accomplished on $5.00 annual dues.)

The report of the annual election, for president, three vice-

presidents, three managers, treasurer and secretary was then, in the absence of all of the tellers, opened by the Secretary and read as follows:

REPORT OF THE TELLERS OF ELECTION.

To the American Electrochemical Society:

GENTLEMEN: Following is the result of count of ballots for officers of The American Electrochemical Society:

For President—L. H. Baekeland, 102; W. H. Walker, 71; W. R. Whitney, 27; Jos. W. Richards, 8; C. E. Acker, 7; E. R. Taylor, 3.

For Vice-Presidents—F. J. Tone, 140; Carl Hering, 125; W. D. Bancroft, 119; H. N. Potter, 49; A. von Isakovics, 47; W. H. Walker, 30; S. P. Sadtler, 26; E. R. Taylor, 25; L. H. Baekeland, 19; C. O. Mailloux, 16; C. E. Acker, 12; S. A. Tucker, 10; W. G. Clark, 1; J. W. Richards, 1.

For Managers—E. R. Taylor, 144; W. L. Miller, 79; W. H. Walker, 75; H. R. Carveth, 55; E. A. Sperry, 51; C. A. Townsend, 42; Carl Hering, 32; C. E. Acker, 31; W. D. Bancroft, 29; A. H. Cowles, 28; L. H. Baekeland, 26; F. J. Tone, 14; C. F. Lindsay, 5; W. R. Whitney, 2; H. W. Wiley, 2; S. A. Tucker, 1; A. von Isakovics, 1; C. Baskerville, 1.

For Treasurer—P. G. Salom, 211.

For Secretary—J. W. Richards, 210; H. R. Carveth, 1.

Respectfully submitted,

W. S. FRANKLIN, *Chairman,*
BARRY MACNUTT,
ALBERT G. RAU.

Bethlehem, Pa.,
March 26, 1909.

The Chairman then declared as elected the following:

President (for one year)—Leo H. Baekeland.

Vice-Presidents (for two years)—F. J. Tone, Carl Hering, W. D. Bancroft.

Managers (for three years)—E. R. Taylor, W. L. Miller, W. H. Walker.

Treasurer (for one year)—Pedro G. Salom.

Secretary (for one year)—Joseph W. Richards.

President-elect Baekeland was given the floor and spoke as follows:

"Mr. Chairman and Gentlemen:

"It is hardly necessary to tell you that you have done me a very great honor. I still persist in thinking that there are dozens of devoted members, people who have distinguished themselves in their work, who are better qualified for this honor than I am. I feel that in accepting this kind election I am assuming great responsibility. The Society from its lowly beginnings has reached a point which undoubtedly shows that it is going to become one of the most influential organizations of its kind in the world, and I realize so much the more, at this critical point, when its activities are so varied and so important, that anyone accepting the presidency of the Society takes on very serious responsibilities. I must say, however, that whoever has cast his vote for me, very much against my own will, must divide the responsibility with me; and if at the end of the year I have not made good, gentlemen, and you feel you have some recriminations against me, I am going to divide them with those who have been led to vote for me through too much kindness." (Cheers.)

The business part of the session being concluded, the reading and discussion of papers was taken up. The paper of C. A. Hansen, read Thursday afternoon, was called up for discussion, Mr. Hansen also presenting in connection therewith an *addendum* to his paper. Papers by E. F. Northrup, E. F. Kern, S. A. Tucker and E. G. Thomssen, E. F. Northrup, H. E. Patten and W. R. Mott (presented by Mr. Mott), S. A. Tucker and E. G. Thomssen (presented by Prof. Tucker), W. J. McCaughey, J. A. Yunck, G. A. Hulett, H. E. Patten and W. J. McCaughey (presented by Dr. Guttman), C. I. Zimmerman, and A. P. Stechel (presented by Carl Hering) were communicated and discussed, as printed in full in the Transactions.

The afternoon of this day was begun by the taking of a group photograph, followed by visits to the gate-house of the Ontario Power Co., the power house of the Electrical Development Co., Ltd., the power plant of the Canadian Niagara Power Co., the power house of the Ontario Power Co. and their large transformer station.

The evening was spent around the banqueting table in the spacious dining-room of the Clifton Hotel, 145 being present. After-dinner speeches were made by President Acheson, President-elect Baekeland, Cavalier Ernesto Stassano, of Turin, Mr. Charles Kirchoff, W. D. Whitney, C. F. Burgess, H. B. Coho, and J. W. Richards. Prof. W. D. Bancroft was toast-master.

SESSION OF MAY 8th.

The meeting was called to order at 9 A. M., president E. G. Acheson in the Chair. Papers by A. H. Patterson, C. F. Burgess, L. H. Baekeland, J. W. Turrentine (A Graphite Cathode Dish), S. A. Tucker, W. A. Alexander and H. K. Hudson, C. I. Zimmerman (Properties of Silicon), O. P. Watts and E. R. Suhm (presented by Dr. Watts), F. K. Cameron (presented by C. I. Zimmerman), J. W. Turrentine, L. S. Palmer and R. C. Palmer, W. R. Mott and C. I. Zimmerman [1] (Concentric Tubular Conductors) were communicated and discussed, as printed in full in the Transactions.

The reading and discussion of papers being finished, Mr. Carl Hering moved the following:

Resolved, That the sincere thanks of the American Electrochemical Society be and are hereby extended to

The Canadian Niagara Power Company,
The Electrical Development Co., Ltd.,
The Ontario Power Company,
The International Acheson Graphite Co.,
The Niagara Falls Hydraulic Power and Mfg. Co.,
The Niagara Falls Power Co.,
The Development and Funding Co.,
The Niagara Club,
Messrs. FitzGerald and Bennie, of Niagara Falls,
The Local Committee of the Society,
The Ladies' Committee,

for their courtesy, attention and hearty endeavors to render pleasant and profitable this Fifteenth General Meeting of the Society.

[1] We most regretfully announce that Mr. Zimmerman lost his life by accident one week after the meeting. The manuscript of this paper was taken home by him to make some additions or corrections, and has not been located in time to print in this volume.

The motion being carried by acclamation, President Acheson then called on President-elect Baekeland, who addressed the following closing words to the meeting:

"GENTLEMEN: I shall have plenty of opportunity to make addresses, more really than I would like, during the coming year, so I am not going to take up much of your time, except to call your attention to a matter which ultimately will involve your co-operation.

"I am leaving next week for the International Congress of Applied Chemistry, in London. I have been intrusted, as one of the delegates of the United States Government, to request the chemists of the world to hold the next International Congress, of 1912, in the United States. These International Congresses have become the most serious events in the chemical engineering world. All branches of chemistry, and more especially electro-chemistry, are represented in them. At these congresses are assembled the most prominent people one can easily meet all together at one time at any particular place. It is one of those events which you never forget. I have been fortunate enough to be able to be present at a couple of them, and I think the coming congress in London will be even more important than its predecessors. Just before leaving New York I received official and absolute assurances that our invitation is going to be accepted, and that in 1912 we are going to have the honor for the first time in the history of these chemical congresses, of receiving the chemists of the world right here in the United States. It is an honor which involves, of course, responsibilities and serious work. It is not a matter for the chemists of New York alone, or even of the United States. That event is as international as possible. Papers are read in four languages, speeches are made in all languages; in fact, the proceedings are printed in four languages, and we shall want not only the co-operation of all the sections, and all the subdivisions, and all the members of all the different chemical organizations, but we shall want the entire co-operation of Canada as well as of the United States. I would ask you, gentlemen, as a favor, to distribute the news amongst your friends, and begin to study the matter from now on. I know it is three years ahead, but there is lots of work to do if we are to make this event worthy of the honor which is coming to us."

President Acheson then officially declared the Fifteenth General Meeting of the Society closed.

In the afternoon cars were taken to the plant of the Development and Funding Co., where the Townsend electrolytic chlorine and caustic soda cell was seen in operation; later to the works of the International Acheson Graphite Co., thence to the power house of the Niagara Falls Power Co., and last to the plants of the Niagara Falls Hydraulic Power and Manufacturing Company.

In the evening the Niagara Club tendered members and guests an "open house," which was greatly enjoyed by all who attended.

ANNUAL REPORT OF THE BOARD OF DIRECTORS

To the Members of the American Electrochemical Society:

We submit herewith the annual reports of the Secretary and the Treasurer for the year 1907, the former containing the detailed financial statements of receipts and expenditures.

The increase in the number of members was satisfactory, being over 13 per cent., as against 10 per cent. in 1907. A considerable expenditure for the purposes of the membership committee, made in 1908, is bearing fruit in 1909, the increase of membership in the first three months of 1909 being just equal to the whole increase during 1908. The membership at date of this meeting is, in round numbers, 900, with 50 members elected but not yet qualified by payment of dues, and 50 on the list of applicants to be voted upon this month, so that the number of 1,000 members has been practically attained at this Fifteenth Meeting.

The financial status at the close of 1908 was satisfactory, in spite of an excess of expenditures above receipts of $165 during the year. This excess was made up out of our permanent investment fund, which amounted to nearly $2,000. It is gratifying to report that at the present time this withdrawal from permanent investment has been already replaced and several hundred dollars in excess added to that fund. The deficit for 1908 was mostly due to the distribution to our members of the two largest volumes yet issued by the Society, Volumes XI and XII, containing together 1,025 pages, and entailing printing expenses of over $3,000.

The following are the more important actions taken during the year by the Board of Directors:

The following committee was appointed to represent the Society at a conference of electrical societies called to consider the fixing of the fundamental electrical units: Carl Hering, Chairman; Th. W. Richards, H. T. Barnes and Edward Weston.

Mr. Edward R. Taylor was appointed to represent the Society at the "Governor's Conference," held in Washington, D. C., to consider the "Conservation of Our Natural Resources."

The offer of a prize of $500 by the Pacific Coast Borax Co. was accepted as a trust fund, to be awarded for some improvement in the commercial manufacture of ferro-boron from colemanite by a direct process. A committee appointed by the board drew up regulations governing the competition for and the award of this prize.

Mr. Edward R. Taylor was elected Manager, to fill the unexpired term of Mr. E. G. Acheson, when the latter had been elected President.

The Society has undoubtedly entered upon a period of expansion in usefulness, numbers and influence. Its field is broadening rapidly; it furnishes a common meeting ground for engineers, chemists and metallurgists, electricians and physicists. Its national and international importance are recognized and rapidly increasing.

Given the same unselfish, enthusiastic and united support of its members in 1909 as in 1908, the continued progress of the Society in numbers, influence and usefulness is an assured fact.

EDWARD G. ACHESON, *President.*
JOSEPH W. RICHARDS, *Secretary.*

Niagara Falls, Canada, May 7, 1909.

SECRETARY'S ANNUAL REPORT

To the Board of Directors of the American Electrochemical Society:

GENTLEMEN:—The Secretary's report in 1908 was made to cover the calendar year 1907, and I have made this report to cover the calendar year 1908.

In 1908 the Society held two general meetings, one in Albany,

N. Y., April 30th to May 2d, at which the attendance was 75 members and 60 guests, total 135; and the second in New York City, October 30th and 31st, at which the attendance was 123 members and 68 guests, total 191. At the spring meeting 21 papers were read, and at the autumn meeting 16.

In 1908 there was issued and distributed to our members two volumes of Transactions. Volume XII was of the New York City meeting of October 17-19, 1907; Volume XIII of the Albany meeting of April 30-May 2, 1908. These volumes contained 477 and 548 pages respectively. The Transactions of the New York City meeting of October 30 and 31, 1908, were issued as Volume XIV, March 16, 1909; they contained 274 pages.

The editions of Volumes XII and XIII were 1,000 copies bound in cloth for distribution to our members, 50 extra copies in sheets for distribution in pamphlet form to authors of papers, and 500 copies bound in paper for distribution to the members of the Faraday Society, about half of which remain in stock.

In the fourteen volumes now issued as the Transactions of the first seven years of the Society's activity, there are contained 338 communications, covering 4,592 pages.

Complete sets of all these volumes are still obtainable through the Secretary, but the stock on hand is fast diminishing.

There were on hand, December 31, 1908:

Volume	Bound in cloth.	Bound in paper.	Total.
I	278	8	286
II	202	...	202
III	320	...	320
IV	254	235	489
V	187	235	422
VI	258	242	500
VII	206	248	454
VIII	216	238	454
IX	184	275	459
X	229	258	487
XI	177	262	439
XII	239	266	505
XIII	222	218	440
			5,457

Condition of the Society in regard to membership:

Members January 1, 1908		684
Elected and qualified as members in 1908		135
		819
Resigned in 1908	9	
Deaths	4	
Dropped for non-payment of dues	30	
		43
Members December 31, 1908		776
Net gain in membership in 1908		92

Financial Statement.

January 1, 1908, to December 31, 1908.

RECEIPTS.

Entrance fees	$ 675 11
Annual dues	4.067 64
Advertising	234 26
Sale of publications	582 21
Interest on bank account and investments	92 77
Withdrawal from permanent investment	500 00
Membership certificates	101 11
Rebate on insurance	11 28
	$6,264 38

EXPENDITURES.

Salary, Secretary and Assistants	$ 871 92
Office expenses	263 82
Office printing, stationery and postage	572 80
Postage on Transactions	316 00
Publications (Volumes XII and XIII)	3,018 46
Commission on advertising	45 75
Storage and packing	39 25
Meetings of the Society	397 55
Appropriation to New York Section	136 99
Expenses of Membership Committee	263 06
Rent of safe deposit box	3 00
	$5,928 60

ASSETS, JANUARY 1, 1908.

Cash balance, Jan. 1, 1908—On deposit		$ 107 84
Cash box		50 00
Bonds held by the Society (cost price)		1,948 75
		$2,106 59

ASSETS, DECEMBER 31, 1908.

Cash balance, December 31, 1908—On deposit		$ 443 62
Cash box		50 00
Bonds held by the Society (cost price)	$1,948 75	
Ferro boron prize, held in trust	500 00	
Equity of Society in above bonds		1,448 75
		$1,942 37
Loss in assets for the year 1908		$ 164 22

The loss of $164.22 was actually taken out of permanent investment fund, but has since been replaced. The deficit was due to the publication of the two largest volumes of Transactions yet issued by the Society, and to heavy expenditures at the close of the year by the Membership Committee. That the latter expense was justified is shown by the fact that exactly as many new members were added in the first three months of 1909 as in the whole of 1908. The present status of the Society shows that its finances reached their turning point at the end of 1908, and 1909 will without doubt show a surplus of receipts above expenditures.

The Secretary recommends that the Publication Committee make suitable provision for the large present and prospective increase of membership during 1909 by increasing considerably the editions of Volumes XV and XVI.

JOSEPH W. RICHARDS,
Secretary.

Lehigh University, South Bethlehem, Pa.,
May 1, 1909

TREASURER'S ANNUAL REPORT

FOR THE YEAR 1908.

Balance, January 1, 1908	$ 157 84
Receipts from Jos. W. Richards, January 1, 1908, to December 31, 1908	6,264 38
	$6,422 22
Expenditures, January 1, 1908, to December 31, 1908, as per list	5,928 60
Balance, December 31, 1908	$ 493 62

PEDRO G. SALOM,
Treasurer.

MEMBERS AND GUESTS REGISTERED AT THE FIFTEENTH GENERAL MEETING.

Members.

E. G. Acheson
E. G. Acheson, Jr.
Chas. E. Acker
G. F. Ahlbrandt
L. Albright
Thos. B. Allen
Wm. H. Arison
James Aston
Dr. Leo H. Baekeland
F. H. Banbury
Wilder D. Bancroft
P. P. Barton
J. F. Becker
F. M. Becket
John W. Beckman
F. M. DeBeers
P. McN. Bennie
Sol. D. Benoliel
Edw. R. Berry
Hugo DuBois
Wm. Brady
H. L. Brinker
John W. Brown
C. F. Burgess
J. R. Cain
F. D. Carney
C. F. Carrier
H. R. Carveth
C. R. Cary
Adolph Chalas
D. H. Childs
Camilo C. Cito
W. R. Clymer
Jesse Coates
H. B. Coho
Ed. A. Colby
E. P. Coleman
V. G. Converse
A. H. Cowles
G. E. Cox
Fred Crabtree
H. C. Cridland
E. L. Doty
H. H. Dow
Ervin Dryer
Wm. L. Dudley
O. E. Dunlap
I. R. Edmands
J. W. Evans
F. A. J. FitzGerald
Chas. E. Foster
R. E. Fowler
K. G. Frank
E. Friedlaender
R. Furness
A. E. Gibbs
W. T. Gibbs
I. K. Giles
J. Graham
A. E. Greene
L. F. Guttmann
E. Haanel
C. M. Hall
S. F. Hall
C. Hambuechen
C. A. Hansen
J. L. Harper
F. W. Haskell
D. M. Hepburn
C. Hering
H. D. Hibbard
A. C. Higgins
G. Hinrichs
S. E. Hitt
A. H. Hooker
H. Howard
L. E. Howard
G. A. Hulett
E. J. Hutchinson
D. McIntosh
Alois von Isakovics
Rees James
D. J. Jenkins
Fred. A. Johnson

Members (Continued).

B. Katsura
H. W. Kellogg
Philo Kemery
C. Kirchoff
Wm. Koehler
H. Hughart Laughlin
F. A. Lidbury
A. T. Lincoln
E. S. Lincoln
Jas. MacMahon
P. R. Manahan
Otto Mantius
C. W. Marsh
A. L. Marsh
Jas. G. Marshall
Jno. A. Mathews.
Max Mauran
A. S. McAllister
J. L. Merrill
Wm. F. Meredith
W. Lash Miller
J. W. Mills
H. P. Mills
H. S. Miner
R. Moldenke
G. W. Morden
C. H. Moritz
Henry G. Morris
G. C. Moyer
Henry N. Muller
Wm. E. Nickerson
E. F. Northrup
J. E. Ober
G. Ornstein
R. S. Orr
G. T. Page
C. W. Parkhurst
Chas. L. Parsons
John C. Pennie
Napoleon Petinot
Ross Phillips
O. W. Pickering
Irenee du Pont
J. W. H. Randall
P. P. Reese
R. C. Reed
A. G. Reeve
Jos. W. Richards
H. K. Richardson
A. G. Rodgers
Hugh Rodman
E. F. Roeber
W. Ross
Louis Ruhl
Henry E. K. Ruppel
Chas. J. Russell
Pedro G. Salom
Lewis E. Saunders
Carl G. Schluederberg
Elliott M. Sergeant
J. A. Seede
S. P. Sharples
A. L. Simmers
Louis Simpson
A. W. Smith
Edmund S. Smith
Wm. A. Smith
Wm. L. Spalding
E. C. Speiden
E. A. Sperry
E. C. Sprague
F. A. Stamps
A. Stansfield
E. Stassano
R. H. Stevens
Geo. W. Stone
C. J. Strosacker
Jokichi Takamine
Edward R. Taylor
Chas. E. Taylor
B. F. Thomas
F. J. Tone
S. A. Tucker
W. H. Van Winckel
C. F. Vaughn
F. K. Vial
Anthony Victorin
S. S. Wales
Walter Wallace
Louis E. Ward
Oliver P. Watts
W. S. Weedon
Fred B. Wheeler
E. H. Whitlock
W. R. Whitney
B. Wiley
J. Rattray Wilson
A. M. Williamson
A. J. Woodworth
W. J. Wooldridge
John A. Yunck
Edward Zaremba
C. I. Zimmermann
F. Zimmermann

Guests.

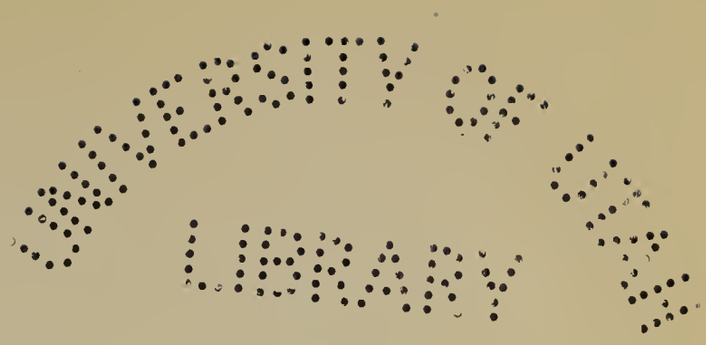
Mrs. E. G. Acheson
Mrs. W. H. Arison
Miss Arison
Mrs. P. P. Barton
Mrs. H. J. Corvil
Mrs. Alfred H. Cowles
Mrs. J. W. Evans
Mrs. W. T. Gibbs
Miss Gibbs
Mrs. F. W. Haskell
Mrs. A. H. Hooker
Mrs. M. L. Hutchinson

Guests (Continued).

Mrs. Alois von Isakovics
Mrs. E. S. Lincoln
Mrs. J. G. Marshall
Mrs. J. L. Merrill
Mrs. Geo. Morden
Mrs. E. F. Northrup
Mrs. O. W. Pickering
Mrs. F. I. du Pont
Mrs. Irénée du Pont
Miss M. Ellen Richards
Florence H. Richards, M.D.
Mrs. C. J. Russell
Mrs. L. E. Saunders
Mrs. E. M. Sergeant
Mrs. Geo. W. Sergeant
Mrs. Wm. A. Smith
Mrs. E. C. Speiden
Mrs. E. C. Sprague
Mrs. G. W. Stone
Mrs. J. Takamine
Mrs E. R. Taylor
Miss E. B. Taylor
Mrs. F. J. Tone
Mrs. C. F. Vaughn
Mrs. S. S. Wales
Mrs. Elliott H. Whitlock
Mrs. A. J. Woodworth
Mrs. Jno. A. Yunck
Miss Agnes Yunck

R. W. Acheson
R. H. Acott
H. G. Akers
H. L. Arnold
J. Watson Bain
W. P. Barba
Geo. T. Barker
J. B. Barned
A. Barton
H. C. Beltz
E. Blough
H. A. Boyd
E. C. Butler
C. H. Calkins
H. B. Carter
R. H. Clayton
Frank N. Coe
Chas. Colne
W. P. Colire
H. J. Corvil
L. B. Coulter
W. N. Crafts
Chas. Crew
R. Cuchens
E. L. Diehl
J. C. Downs
J. A. Durfee
S. Dushman
Theo. W. Elliott
S. W. Farnham
G. C. Furness
E. T. Gehckens
D. W. Gillette
Ainslie A. Gray
Frank E. Hall
T. J. Hancock
W. N. Hanlan
Wm. Smith Harvey
John Hay
O. S. James
A. B. Jones
Phil. H. Jordan
E. J. Kenny
E. D. Kingsley
K. Knudsen
E. F. Lake
Wm. E. Lambert
F. M. Lane
Horace W. Lash
J. D. Lewis
Henry B. Logan
R. A. Luther
R. L. MacDonald
F. Mauelen
L. M. McDonald
Robt. J. McNitt
K. J. McRae
E. D. Miller
Kenneth B. Millett
J. H. Morice
J. M. Muir
Albert E. Playter
Francis I. du Pont
I. La Verne Powers
K. C. Randolf
L. V. Redman
Jno. C. Reed
E. I. Reilly, Jr.
Wm. A. Ritenburg
Edw. J. Schneider
Henry F. Schmul
W. H. Scott
H. F. Sill
V. Skillman
Chas. V. Slocum
Y. C. Smith
E. C. Spurge
Aug. Stillesen
Wm. F. Stuart
J. L. Stuart
G. M. Sturgess
J. B. Tindall
James Tinlin
C. A. Tryon
T. E. Tynes
G. B. Waterhouse
F. B. Weaver
R. F. Webber

The Presidential Address, delivered at the Fifteenth General Meeting of the American Electrochemical Society, at Niagara Falls, Canada, May 6, 1909.



THE ELECTROCHEMIST AND THE CONSERVATION OF OUR NATURAL RESOURCES

By Edward G. Acheson.

When President Roosevelt declared, from the stage of the Belasco Theatre, at Washington, to the conferees of the joint conservation conference there assembled December 8th, 1908, that we, the people of the United States, were the first to take a national attitude toward the conservation of natural resources, I experienced a thrill of pride in being one of this great people. A profound sense of pleasure was felt in the realization that we were now great enough to call a halt in the heedless consumption of the world's stock of necessities, rich enough to construct great works for the attainment of that end, scientific enough to create artificial duplications of the natural and add to the list of materials nature has provided for man's use, and, lastly, humane enough to devote some thought, work and resources toward providing for our unborn posterity.

At the succeeding sessions of the conference there was a double definition given to conservation of natural resources—the preservation of these valuable assets of the country for posterity, and, again, the energetic and economic, although conservative, utilization of the world's good things by the people of to-day. Much stress was laid, for instance, upon the great advantages of a national movement for the use of the natural resource, water, for the carrying to and fro of the internal commerce of the country. It was considered advisable to issue vast sums in bonds, that our children and our children's children might participate in the obligations involved in this great work of, as it was stated, saving us some millions of dollars annually in transportation, these great waterways remaining, of course, for these children to enjoy and profit by in return for their bond payment.

A matter of much regret and surprise was the failure of this great representative body of citizens to devote some time to the actual conservation of our perishing resources. To fail to grasp the grand opportunity of this great nation, the first to suggest the movement, to omit to lay at least the foundation of a structure that will be erected by some nation, to last as long as life exists on earth—the real conservation of nature's exhaustible resources by the scientific use of her inexhaustible ones—should surely be a matter of regret and mortification.

To fully utilize the natural inexhaustible resources should and would be a matter of extreme pride to the present and future generations of citizens of the United States, but to do that and to simultaneously conserve the natural exhaustible resources would be an example to the entire civilized world, and to be the first people to do so would, for all time, sustain the American people in their present position of progressiveness.

By suppressing selfishness, corporate greed and personal aggrandizement, the people of America are to-day capable of building as no people have built, and this without permanent cost. They have within their broad country all that is necessary to carry this grand possibility to fruition. This can be accomplished through earnest co-operation between bond issue, utilization of inexhaustible resources, and the world's present scientific knowledge, which we may hope will be enhanced in value by new light yet to come through the channels opened, and to be opened, by electrochemistry.

The executive department of the United States has pledged itself to the issue of bonds for the development and utilization of the natural resource, water. This development and utilization should be broadened; in fact, it should begin with the construction of great water powers, with which the electrochemist could produce substitutes for, and, in some cases, improve upon the natural exhaustible resources, and, in other instances, produce within the country products which are now being bought abroad at an annual expenditure of many millions of dollars.

This last mentioned condition is strikingly illustrated by sodium nitrate, the commercial product more generally known as Chili saltpeter.

The world has been depending on Chili saltpeter for the nitro-

gen essential for fertilizers and explosives. It is mined only in Chili and Peru. The world's consumption during the year 1907 amounted to 1,662,000 long tons; the imports into the United States exhibited a very steady increase from 147,495 tons in 1898 to 364,610 tons in 1907. During the same period the price increased rapidly from $15.58 in 1898 to $40.71 per ton in 1907, and during the decade the total value imported was $80,916,224—a very large sum of money to send out of the country; but let us examine the prospects for the future.

It is fair to assume that the consumption of nitrate will continue to increase for the next twenty years as it has during the ten years just passed, and if that be the case, we have the following remarkable figures before us: The importation in the year 1926 will be 798,840 tons, and the average annual importation for the twenty years ending with that date will be 581,725 tons, giving as a total amount imported 11,637,500 tons. As will be seen from the statistics of the past, the value per ton has risen in a remarkable manner, due largely to the nearly exhausted condition of the Chili deposits, but in view of the fact that electrochemistry has mastered the problem of fixation of nitrogen, it is not at all likely that the price will continue to materially advance, and for the purpose of my estimate I will assume there will be no further advance. If the importation of nitrate continues to increase as during the last ten years (and this would be necessary to meet the growing demands of agriculture) and the same price be paid as in 1907, there will, during the twenty years ending with 1926, be sent out of the country no less than $473,640,495, or enough to dig the Panama Canal and leave a good balance to the country's credit.

Up to the present there has not been the means of avoiding this outflow of money, but such is not now the case. Electrochemistry has solved the problem of fixing free nitrogen into definite stable compounds with other elements by at least two commercial methods. Nitrogen is one of the most widely diffused of the elements, constituting four-fifths by volume of the air, and Dr. Albert R. Frank, in a paper read before the Faraday Society, pointed out that the amount of it contained in the still air covering each nine acres of the surface of the globe is equal to that contained in the Chili saltpeter exported from South

America in the year 1907. There is more nitrogen superposed on every two square acres of United States soil that was imported into the country as saltpeter in the year 1907. From this ever-present natural resource we can, by means of cheap power, obtain our nitrogen fertilizer, cyanide for gold extraction, and have also within the country a source of fixed nitrogen for explosives, thus being freed from possible helplessness in the event of war cutting off the foreign supply.

The problem is now receiving the close attention of the scientific and financial world. A hydro-electric power plant of 53,000 horse-power has been successfully operating for some time on the fixation of atmospheric nitrogen in Norway, and it is now to be increased by 200,000 horse-power; and another plant of 120,000 horse-power is about to be erected in Norway, while Canada is preparing to set 60,000 electrical horse-power to work on the same line. The cost of water power for these several plants is, or will be, from one-fourth to one-half what similar power would cost in the United States. After reviewing the developments in Norway, Dr. Frank states: "Norway saltpeter is destined to remain the only direct competitor of the Chilian variety." Will Americans patiently see this prediction fulfilled?

The manufacture of saltpeter, at a cost to compete with the Chili product, is a typical example of the conservation of our inexhaustible resources, under one of the definitions as propounded at the joint conference. We have as ready access to nature's store of nitrogen as the people of Norway, millions of available water power, and an immensely greater internal market for the product.

The conservation of the exhaustible resources is perhaps of less importance to the present generation than the utilization of the inexhaustible resources, but immensly more important to posterity. As examples, we will take the two natural exhaustible resources, coal and oil.

Carbon is, I believe, as important to man as any other one element, entering constantly into his manufacturing and commercial life. Nature provided a certain amount of carbon in fixed chemical combinations, as our natural resources, coal and oil, which we have been consuming and wasting in a prodigal manner. The total amount supplied by nature is limited. Our

experts now know approximately the amounts we have in stock and how long they will last, for end they surely will.

These two resources are mainly being consumed in the production of what the scientific world calls "wave motions"—light or heat waves, both essential to our way of living, either for the production of light to our eyes, warmth to our bodies, or heat for our domestic, manufacturing and transportation uses. There are other and perhaps unavoidable uses of our fixed carbon, as, for instance, a reducing agent in metallurgy, the production of power for ocean-going vessels, the making of carbides, etc. But for that portion of the carbon consumed in producing wave motion—and it represents a large part of the total—a ready and everlasting substitute is to be found running to waste in all sections of our great country, our natural resource, water, which can be made inexhaustible, and whose power can be converted into electricity, an ever-ready servant for the production of wave motions and mechanical power for manufacturing and transportation.

The most logical course to pursue in the conservation of natural resources is evidently to begin with the forest, as is now being done by the efficient Forest Service of the United States Government, in order to promote the continued flow of the waters; next the impounding of the waters when in flood, then the construction of great hydro-electric power plants, and finally the creation of waterways. The electric power would furnish the means for transportation, whether by railway or water, and electric current for lighting, heating and electrochemical uses. The waterways would lend themselves to irrigation. Such a project carried to completion would usher in the Electrochemical Age and actually conserve our natural resources of all characters.

Electrochemistry is undoubtedly destined to play an important rôle in the conservation of our natural resources. In its more modern form, and especially as applied to metallurgy, it is still young, becoming prominent in 1888 at the time of the beginning of what is now one of the largest electrochemical industries, the manufacture of aluminum by electricity. Within the twenty years since that date, great strides have been made, a number of chemical and metallurgical processes having been converted into electrochemical and electrometallurgical ones in a very suc-

cessful way and to the advantage of the industrial world, while at least five new materials, previously unknown, are now sold in the world's markets, they having been made possible of production by electrochemistry.

Electrochemistry is, in fact, a creator, transforming the cheap and, perchance, useless wastes into products of value. It works either with the silent invisible electric current, or by the stress of heat. It lends itself to the ready production of temperatures from that of the atmosphere to the highest attainable on earth, one in which the metals and rocks disappear in vapor. It is creating a new synthetic chemistry, and provides the most perfect means known for obtaining high purity of some elemental substances. It tears asunder the elements as joined by nature and rearranges them under man's guidance. Thus it has made ordinary sand react with carbon and form the well-known product, carborundum. In another case lime and carbon are made to react in the electric furnace to form the valuable product, carbide of calcium, now well known as the source from which our familiar acetylene light is obtained. In another instance it converts "culm," the waste material of the anthracite coal mines, into valuable graphite. Again it has enabled us to extract from sand metallic silicon, which has found a place in our arts and manufactures. In still another instance it fuses in the electric furnace the soft, amorphous bauxite into "alundum," suitable for use as an abrasive and refractory material. Electrochemists are now earnestly at work on problems of even greater magnitude than any of these, as, for instance, the electrometallurgy of iron and steel, and all this without calling upon our exhaustible natural resources, but by the utilization of the inexhaustible energy of our waterfalls.

The first hydro-electric power plant of considerable magnitude in America was put into operation at Niagara Falls, in the fall of 1895, since which date an electrochemical center has developed at that point, and there is now approximately 125,000 horse-power being utilized in the work of producing phosphorus, carbide of calcium, alundum, caustic alkali, bleaching powder, metallic sodium, aluminum, metallic silicon, carborundum, artificial graphite, chlorate of potash and other products, the united values of their annual production amounting to many millions of dollars.

These Niagara products may, to the great industrial world, seem small, but they have been developed within a few years, they cover a varied field, and they are but a promise of the future development when we have cheaper power, they being produced with power costing three to four times the price of similar power in Norway. Were these products being made by any means other than water power, serious inroads in one of our natural exhaustible resources, carbon, as it appears in coal and oil, would be occurring.

Having thus reviewed the conservation of our natural resources and the part electrochemistry is now taking in this all-important work, we will, I think, profit by the study of the *personnel* of the electrochemists, whose duty and pleasure it shall be to explore and develop this magnificent field—a field for work without equal in extent, richness and fascination, and with possible rewards as great as any heretofore paid to man. The field is much too extensive and rich to be monopolized by any one—or more—of the professions as heretofore defined and recognized. The work to be performed will largely consist of the development of hydro-electric power, experimental research, and application of results obtained, and will call for the earnest co-operation of the chemist with engineers in the various recognized engineering lines.

It is in the experimental researches that perhaps the greatest interest will center, and it will not infrequently happen that the investigator will secure a prize he was not in search of. He should be a close observer of small effects, ever on the watch for the unexpected, and he will frequently turn what to the careless observer might appear a failure into a success. But few broad, straight, open roads will be found; on the contrary the ways are narrow, crooked, and contain many, very many, obstructions. In many cases these scarcely discernible trails divide into blind, fruitless paths, leading one astray, and happy is he who selects the right one and attains the goal.

A cause of much gratification has been the large number of engineers who have joined our society during the year now closing, and, speaking for the society, I welcome them most heartily. I hope and sincerely believe they are now part of a great national force that is destined to be one of if not indeed

the greatest of all influences in the shaping and developing of the future progress and welfare of the world.

The Government will, I think, ere long recognize electrochemists, and our society in particular, as an important factor in the industrial and commercial life of the nation and as a means of materially conserving the interests of posterity. It may be that it will in time see the advisability of establishing a department devoted to these interests. Even now an earnest movement is under way for the establishment of a Department of Mines. It is not at all unlikely some of those now present will be still active in our society when a Department of State will be created for the Utilization and Conservation of our Natural Resources, in which department, and its work, Electrochemistry will be the principal factor.

A paper read at the Fifteenth General Meeting of the American Electrochemical Society, at Niagara Falls, Canada, May 6, 1909, President E. G. Acheson in the Chair.

THE ELECTRIC SHAFT FURNACE[1] OF THE AKTIEBOLAGET ELEKTROMETALL, LUDVIGA, SWEDEN.

By Dr. Eugene Haanel.
Director of Mines, Department of Mines, Ottawa.

The conditions governing the utilization of the raw materials necessary for an iron industry in Sweden are similar to, and in many respects identical with, those existing in several of the provinces of the Dominion of Canada. In Sweden, owing to the absence of metallurgical coal necessitating the importation of all coal for this purpose, charcoal is the fuel chiefly used. These are precisely the conditions prevailing in the central provinces of Canada, where the absence of coal demands either the transportation of fuel from the far east or west, or else the importation of fuel from the United States. In many cases the cost of the metallurgical fuel is too expensive to allow the establishment of a successful iron industry. In consideration of these conditions, Canada, and latterly Sweden, have interested themselves in the solution of the problem of economically reducing their ores by the electric process.

In the experiments made at Sault Ste. Marie, under Government auspices, the feasibility of applying the electrothermic process to the reduction of iron ores was demonstrated, and the output of pig iron in tons per horse-power year, which could be expected with even an experimental furnace of small capacity, such as that used at Sault Ste. Marie, determined. It now only needed the construction of a furnace which could be economically and successfully used in practice to place electric smelting on a commercial basis. The depletion of the funds available for the prosecution of the above experiments precluded any further

[1] Continental Europe calls our "blast furnace" the "high furnace," and so with them the term "electric high furnace" has a distinct appropriateness and significance. With us it would not, and therefore we coin the term used above. "Electric blast furnace" would be a solecism.

experimentation with a view of solving this problem, although some work in this direction was commenced.

This work was, however, taken up by three Swedish engineers, Messrs. Grönwall, Lindblad and Stalhane, who were ably assisted by the ironmasters of Sweden, but more particularly Mr. Ljungberg, director of the Stora Kopparbergs Bergslags Aktiebolag, at whose works the many furnaces designed by them were erected. Since the electrometallurgy of the reduction of iron ores had already been established, these inventors concentrated their attention on the solution of the problem of constructing a thoroughly practical and commercial furnace, along the lines suggested in the report on the experiments conducted at Sault Ste. Marie, page 92, viz.:

(1) The top of the furnace requires to be modified to permit of the application of labor-saving machinery for charging.

(2) Provision requires to be made for the collection and utilization of the carbon monoxide produced by the reduction of the ore. This involves also the protection of the charcoal of the charge from combustion on the top of the furnace.

(3) The regulation of the electrodes should be effected automatically.

(4) The shaft containing the charge should be sufficiently high to permit the heated CO to effect maximum reduction of ore, and the electrode should not be immersed in this shaft, but contained in a side chamber supplied with the charge from the main shaft.

Over two years were devoted to designing and constructing furnaces of different designs, the experience gained in the preceding furnaces being utilized in the design and construction of the succeeding ones. In all, seven furnaces were erected and tested, and about $102,000 spent on this work before they constructed a furnace which, in their opinion, was practical and commercial.

When the Swedish inventors were satisfied that they had constructed a thoroughly commercial furnace, I was tendered an invitation to witness a run of long duration, which was to begin some time in December.

Just as the steamer was leaving the pier, I received a cablegram from Sweden, stating the impossibility of making the con-

Legend

Ordinary Brick Fire Brick Magnesite

templated trial, due to lack of water, but as it was then too late to cancel my passage, I decided to make the trip and obtain as much information as possible concerning the furnace.

On my arrival in Stockholm, I was met by Mr. Grönwall, the director of the firm Aktiebolaget Electrometall, and it was then decided that we should go to Falun and place before Mr. Ljungberg the great importance to Sweden, as well as other countries, of carrying out the contemplated trial run. As a result of this conference, Mr. Ljungberg very generously allowed the use of power to operate the furnace for twelve days.

The very limited time allowed for the trial precluded absolutely the possibility of ascertaining the output of pig iron per electric horse-power year with this furnace, since the time necessary for heating a furnace of this size and bringing it to its normal working condition would be about three weeks, especially since the masonry was new and damp and a more rapid heating could only be accomplished with the risk of damaging the walls and lining.

Description of the Furnace.

It will be seen from the figure, which is a vertical section, that the furnace consists of an upper part—the shaft—and a lower part corresponding to the hearth of an ordinary blast furnace.

The hearth, or melting chamber, is made in the form of a crucible, and is covered with an arched roof provided with openings for the reception of the electrodes and charge. The walls and roof are lined with magnesite brick.

For the purpose of so distributing the charge in the melting chamber that a free space is always maintained between the linings of the roof and walls, the electrodes and the charge at those places where the electrodes enter the melting chamber, and also to support the charge, the lower part of the shaft is constructed in the form of an inverted, truncated cone.

This form was given to the lower part of the shaft in consequence of experiments made by the inventors, which demonstrated the fact that the upper surface of the column formed by the materials charged into the furnace will assume a definite angle, viz.: 50° to 55° to the vertical, when these materials, crushed to normal size and at the same temperature as that existing in

the melting chamber, are allowed to fall through a circular aperture into a free space. In the drawing the slope of the column just referred to is shown by dotted lines.

The contracted neck of the shaft is placed over the opening provided in the arched roof of the melting chamber for the the introduction of the charge, but is not supported by it, the entire weight of the shaft being supported by a system of six cast iron columns symmetrically arranged around the furnace.

The electrodes enter the melting chamber through the openings provided in that portion of the roof which does not come in contact with the charge, and pass into the charge at the slope formed by the materials composing the charge, as described above. This arrangement constitutes the most important factor in the construction of the furnace, owing to the fact that earlier experiments have conclusively proven that it is impossible to use in practice, constructions in which the charge and brick work come in contact with the electrodes at those points where they enter the melting chamber, since, in such cases, the elevation of the temperature at the brick work in the proximity of the electrodes is so great that the most refractory materials that can be employed for the lining are rapidly destroyed, even when the electrodes are cooled by means of water jackets.

For the purpose of cooling the brick work composing the lining of the roof of the melting chamber, thereby increasing its life, three tuyères are introduced into the melting chamber through which the comparatively cool tunnel-head gases are forced against the lining of the roof into the free spaces. This gas absorbs heat from the exposed lining of the roof and walls and the free surface of the column formed of the materials composing the charge, thus effectively lowering the temperature of the roof and exposed walls. No heat is lost, however, by this cooling or lowering of temperature, since the heat given up by the linings of the roof and walls to the comparatively cool gas introduced through the tuyères is imparted in passing upward through the shaft to the cooler charge in the shaft. This not alone effects a better utilization of the reducing power of the CO, but produces also a better distribution of heat throughout the charge of the shaft than in furnaces of former construction.

The tuyères are provided with peep-holes, covered with mica,

157543

through which the interior surface of the arched roof can be observed. By this means a judgment may be formed of the quantity of gas required to be circulated to effect proper cooling.

Electrodes.

A three-phase current is supplied to three electrodes, which are built up from two carbons, 11 inches square and 63 inches in length, making the total cross-section of the built-up electrode 11 by 22 inches. The electrode holder is made of a strong steel frame, which forms a support for the wedges, by means of which the copper plates conducting the current from the copper cables are pressed against the electrode.

The electrode is clamped in the steel frame mentioned above, and slides on two guides, which serve the two-fold purpose of keeping the angle of inclination of the electrode to the vertical constant and relieving the arched roof of any undue strain which would arise from the weight of the electrode, if improperly supported. A steel cable, secured to the top of the electrode holder and passing over a system of guiding wheels or pulleys to the drum operated by the hand wheel on the switch-board, serves to lower and raise the electrode by winding or unwinding the drum.

In order to protect the parts of the electrodes outside the furnace from the oxidizing action of the air, a suitable covering is provided.

The water-cooled stuffing boxes, through which the electrodes enter the melting chamber, are provided with special devices (not shown in the drawing) for preventing the gas under pressure within the melting chamber from leaking around the electrodes.

The shaft, as mentioned before, is supported by an iron structure resting on six cast iron pillars arranged symmetrically around the furnace. To prevent the pillars from being cut off in case of the molten iron accidentally finding its way to them, the lower parts are protected by sand enclosed in a sheet iron casing.

With this construction it is possible to repair or replace, without removing the shaft, those parts of the furnace which are most likely to need repairs, viz., the lower part of the shaft and the melting chamber.

In order to collect the gases for utilization for various purposes, and also to protect the charcoal from combustion, the top of the shaft is closed by an iron cover, which is provided with a charging bell, and to prevent the possibility of gas explosions from air entering the shaft, the charging bell is covered by means of a cap of sheet iron specially constructed for this purpose, when a charge is being introduced. To prevent excessive pressure in the interior of the furnace, a pipe, provided with a loaded self-closing valve at its upper end, conducts the gas generated in the furnace, when the pressure reaches a certain point, to apparatuses for its utilization or to the open air.

Object of the Experimental Run.

The following is a brief summary of the points which the trial was intended to elucidate:

First. Whether undisturbed and uniform working without troublesome regulation of the electrodes could be obtained.

Second. Whether great variations in the consumption of energy would occur.

Third. Whether the free spaces within the melting chamber would be maintained with a shaft considerably higher than in the furnace of former construction.

Fourth. Whether the contraction of the shaft would prevent the charge from sinking uniformly or cause hanging.

Fifth. The durability of the arched roof and the possibility of cooling it by means of the circulating gas.

Trial Run.

The iron ore used had the following composition:

Fe_3O_4	66.46%
Fe_2O_3	21.21%
MnO	0.30%
MgO	0.98%
CaO	3.84%
Al_2O_3	1.07%
SiO_2	3.16%
P_2O_5	2.34%
S	undetermined
Metallic iron	62.96%

During the first part of the trial, coke containing 85 per cent. C and 0.55 per cent. S was used. This, however, had been exposed for a long time to the open air and rain, which made its percentage of moisture unusually high. During the latter part of the run, charcoal was substituted.

The iron and slag were tapped through the same tap-hole, but no difficulty was encountered in separating the iron from the slag after cooling.

The voltage maintained during the entire run was about 37, while the amperes on the three electrodes were between 6,000 and 7,000. In my opinion, the power supplied was far too small for a furnace of this size, and in the future trials arrangements are being made to employ a larger amount of energy.

During the first part of the trial one of the cast iron stuffing boxes for cooling the electrodes was observed to be leaking slightly, but towards the end of the run this leak became so serious that one of the electrodes had to be uncoupled and the furnace was run with only two electrodes.

This accident would never have occurred if the castings had been properly tested, but owing to the very limited time allowed for the trial and the fact that the furnace was entirely new, the different castings were assembled without first being tested.

Notwithstanding these great disadvantages, the output steadily rose from 0.744 metric tons per electric horse-power year in the second casting to 2.44 tons in the sixth casting, when it suddenly dropped in the seventh casting to 1.12 tons per electric horse-power year, owing to the large amount of water escaping into the melting chamber, which finally necessitated the uncoupling of one electrode.

Even while running with two electrodes the output rose to 3.16[1] tons per horse-power year, from which it is reasonable to assume that a better output than that obtained with the small and experimental furnace employed at Sault Ste. Marie could be realized with this furnace.

The consumption of carbon per long ton of pig iron produced

[1] 0.744 tons per electric horse-power year = about 2.00 tons per 1,000 horse-power days.
2.44 tons per electric horse-power year = about 6.68 tons per 1,000 horse-power days.
3.16 tons per electric horse-power year = about 8.65 tons per 1,000 horse-power days.

was 605 pounds. This might be further reduced when the furnace is working normally and the gases circulated as previously described. However, this consumption of carbon must be considered extremely satisfactory.

The consumption of electrodes per long ton of pig iron produced could not be determined, on account of the short duration of the trial. According to former tests, however, this may be placed at 11 pounds per metric ton (2,200 pounds) pig iron.

Summary.

The trial run was conducted for the purpose of elucidating the points previously mentioned, and the following is a summary of the observations bearing on these points:

First. It was observed that the furnace operated uniformly and without trouble of any kind, and that the electrodes required absolutely no regulation, in one case, for five consecutive days. In any case the only regulation required is that corresponding to the consumption of the electrodes, and is necessary only once a day, and sometimes not for much longer periods. On account of this, expensive regulation can be dispensed with.

Second. During the short trial, even though the furnace did not approach its normal working condition until towards the end, it was observed that the consumption of energy was remarkably uniform, on account of which this furnace would constitute an ideal load for a power station.

Third. Free spaces were maintained between the linings of the roof and walls, the electrodes and the charge at those points where the electrodes enter the melting chamber.

Fourth. It was found that the charge did not jam in the lower contracted neck of the shaft, as had been feared, but moved with regularity into the melting chamber.

Fifth. Although the gases generated by the reduction of the ore were not circulated through the cooling tuyères, as previously described, until near the end of the trial run, it was demonstrated that the lining of the roof of the melting chamber was effectively cooled by this means.

To conclude: I have presented to you a very short outline of the examination which I made of the electric shaft furnace in Sweden. I beg to say that since I have only as yet privately

informed the Government of the results of this examination, and no publication has yet been issued from my office, if you were to attempt to ask certain questions, I am very much afraid I should not be able to answer them for the simple reason that it might lead me into expressions of opinion which I am not now at liberty to give.

The furnace was designed by the inventors to have a capacity of 750 horse-power. When I examined it, however, I expressed the opinion that the furnace was altogether too large for the energy employed, and that at least 1,200 to 1,500 horse-power should be used with this furnace. In view of this opinion, the inventors intend to rearrange their electrical plant, rewind their transformers, and enlarge the openings for the electrode, so that they may be able when the run commences again, about the middle of May, to employ at least 1,200 horse-power.

I might say that I pointed out to the inventors that this construction of the lower part of the shaft would likely produce hanging of the charge, and that it would require poking. This the inventors had evidently also feared, since poke-holes had been provided to facilitate the descent of the charge should hanging occur.

The circulation of the gases will be employed throughout the new experiments, and I have every reason to believe that this new series of experiments will demonstrate that the melting chamber will maintain itself for long periods without repair, and that the output will be such that doubts regarding the economic production of pig iron by the electric process will be set at rest.

A paper presented at the Fifteenth General Meeting of the American Electrochemical Society, at Niagara Falls, May 6, 1909; President E. G. Acheson in the Chair.

ELECTRIC FURNACE PIG IRON IN CALIFORNIA.

By P. McN. Bennie.

The industry of producing pig iron in blast furnaces naturally segregates into certain neighborhoods, for reasons that are well known, one of the most important of which is contiguity to fuel supply. Changes in conditions have sometimes resulted in the abandonment of existing plants, or the erection of new plants at new locations, the reasons therefor being equally well recognized.

It is not pretended that the production of pig iron in electric furnaces is now or ever will be economically possible everywhere, for it is subject to the same governing influences as the older industry. The necessary conditions are known, can be definitely described and shown to exist at certain points in this country.

That such an industry is as yet only potential may be attributed to the lack heretofore of an entirely suitable instrument or apparatus, in the way of a furnace, fit for extended campaigns and rough handling; a practical rather than a merely feasible apparatus.

Several serious attempts to develop such an apparatus are now being made, however, with encouraging results. One of these is in California, an account of which will follow this introduction.

During a recent visit to California the author had an opportunity to study the local situation pertaining to the iron industry. Conditions at some Pacific Coast points are peculiarly favorable to electric furnace treatment of iron ores. The present market there is not less than 150 tons a day, the supply being either imported or brought a long distance by rail. Some foundries even go to the extent of melting promiscuous scrap in cupolas. Pig iron brings $9.00 to $10.00 the ton above Pittsburg base, market quotations varying from $23.00 to $26.00 the ton, whether of domestic or foreign origin.

Conditions are not favorable to the operation of a blast furnace to fill this demand. While iron ores might be had at reasonable rates the carbon problem is serious. The only plentiful fuel is California asphaltic petroleum which cannot be used for the purpose. Metallurgical coke brought from the East by rail would be out of the question, while imported coke is not only high in price but irregular as to supply, and therefore variable in price. The California demand for coke is met by importation in cargo from Germany, Belgium and Australia. The coke is bid for upon arrival, hence the irregularity both as to price and supply. The price may be anywhere between $10.00 and $13.00 the ton. Therefore a blast furnace plant would be an investment of uncertain value.

With electric smelting of iron ores, the cost of carbon becomes of less importance, the quantity used being only about one-third that required for the blast furnace. If now we could cheaply assemble iron ore, limestone and electric power at one place, we could afford to use coke or charcoal at a price that would be prohibitive so far as a blast furnace is concerned.

Such conditions may be found at several places in California, within easy reach of the principal market. One such location has been chosen for exploitation by the Noble Electric Steel Co. I had intended to contribute a paper on this company's activities, but recently Prof. Dorsey A. Lyon, General Manager of the Company, consented to prepare an account for us, which I am pleased to substitute for my own as coming directly from those actually doing the work, and, therefore, more in consonance with the original intent of this symposium.

While Prof. Lyon does not refer to it, the experimental 160 kw. furnace was run for a period of forty days, during which time data were gathered to be used in the design of the present 1,500 kw. furnace. The results thus experimentally obtained make it not unreasonable to expect a power consumption around 0.25 horse-power year per ton. Without allowing anything for by-products, charcoal will probably cost $9.00 per ton, of which one ton should be sufficient for about 3 tons of pig iron.

If the figures obtained with the smaller furnace can be realized in the 1,500 kw. furnace, the cost of pig should be in the neighborhood of $15.00. The freight to San Francisco should

not exceed $3.00 per ton. When it is considered that the product will be charcoal pig iron, that should command a higher price than ordinary blast furnace pig iron, there seems to be a comfortable margin of profit for the manufacturer.

Another point not touched upon by Prof. Lyon is that such high grade pig iron, coming from the electric furnace in a molten state, would be most desirable starting material for steel. The liquid metal could be tapped into a second electric furnace and refined to steel, particularly in view of the very pure iron ore available. Or, a modified method like the Lash process could be used. The added expense would be less than the increased value of the product, so there would be a distinct gain in this operation for the manufacturer.

The detailed description will be given in Prof. Lyon's paper.

FitzGerald and Bennie Laboratories,
Niagara Falls, N. Y.

DISCUSSION.

MR. HENRY D. HIBBARD: This question of "year" that is used in connection with this work, I think, ought to be amplified as to whether or not it is the full year of 8,760 hours, or something else. I, myself, in figuring on the question of electric steel, have used the year of 6,500 hours starting at 7 o'clock Monday morning, and running until 5 o'clock Saturday afternoon, for fifty weeks. That totals up to 6,500 hours. It may not be so very important in the case of a water power, where the only extra expense of those extra hours will be the attendance, but if your electricity is to be generated by steam, by the combustion of fuel of any kind, then each hour is expensive, and it becomes important to know how many hours are included in the year when you speak of a certain yield per year of output.

MR. BENNIE: The usual "year" of 8,760 hours was used in my paper and that of Prof. Lyon which follows.

A paper read by Mr. P. McN. Bennie, at the Fifteenth General Meeting of the American Electrochemical Society, at Niagara Falls, Canada, May 6, 1909; President E. G. Acheson in the Chair.

THE NOBLE ELECTRIC STEEL CO'S PLANT.

By Prof. Dorsey A. Lyon.

I will not attempt to present an exhaustive paper on the subject of smelting iron ores by electricity, nor deal with the technical side of the matter. I simply wish to let it be known that such a plant exists in the United States, and to give representation to our country as among those in which the problem of the reduction of iron ores in electric furnaces is being studied. The above named plant is situated at Heroult, Shasta Co., California, and the writer is general manager of the company.

The history of this plant is somewhat as follows: For twenty-five years or more a company known as the Shasta Iron Company has owned a deposit of magnetite, located about seven miles from the mouth of the Pitt River, in Shasta County, California. The ore is a very pure magnetite, having on an average the following percentage composition:

Fe	69.90	Fe_3O_4....89.4 Fe_2O_3.... 7.3
MgO	0.10	
MnO	0.18	
SiO_2	2.40	
P	0.011	
S	0.009	

It occurs at the contact between limestone and diorite. Illustration 1 shows this contact plainly. The ore body is remarkably uniform, a series of twenty samples, taken over a cut 60 by 40 feet, giving the following iron content:

Maximum	70.5 per cent. iron.
Minimum	68.8 per cent. iron.
Mean	69.7 per cent. iron.

Ill. 1.—Showing Contact Between Limestone and Diorite; Magnetite Deposits on the Right.

The limestone is also of excellent quality, having an average composition of:

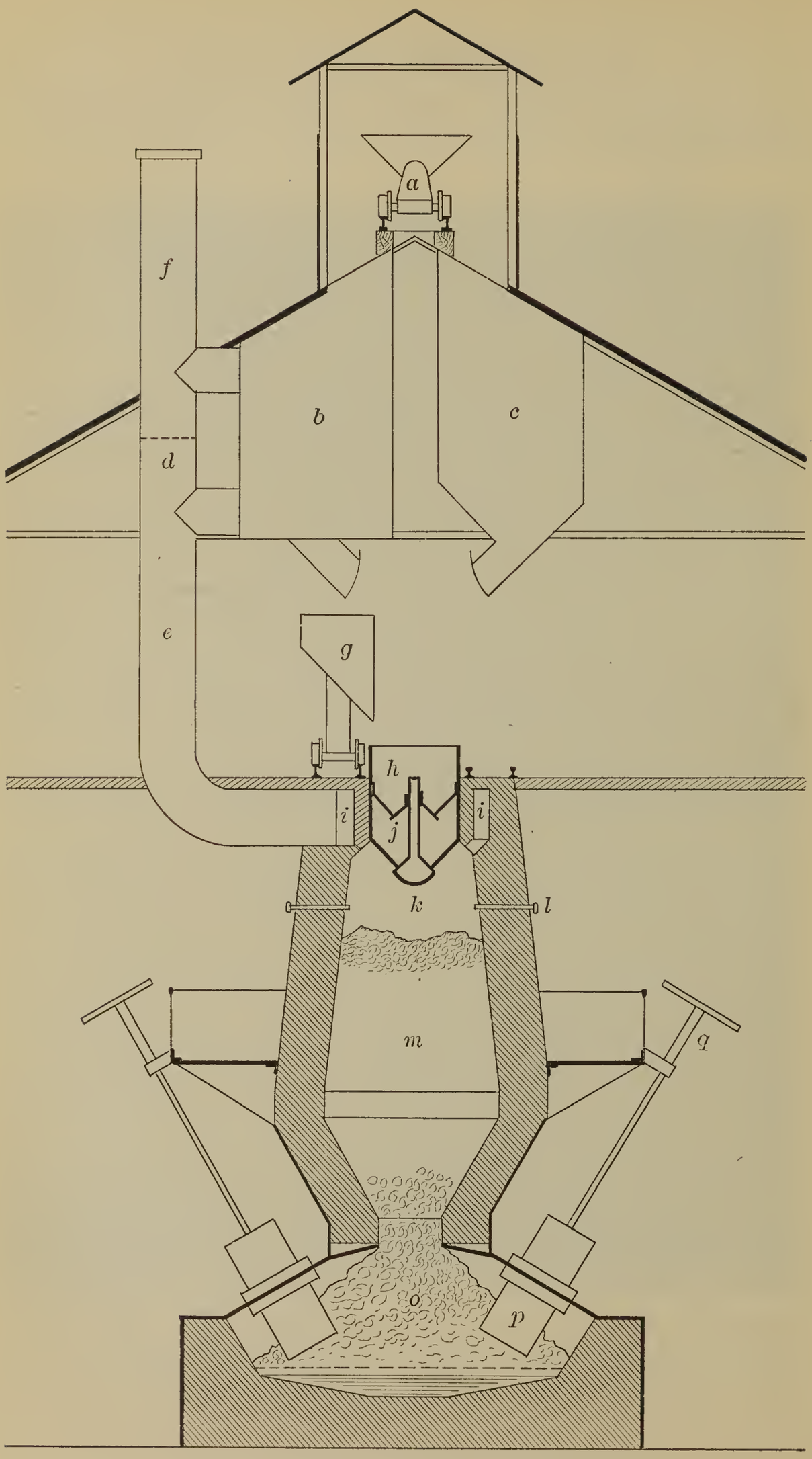
SiO_2	1.20 per cent.
Al_2O_3	0.50 per cent.
MgO	1.10 per cent.
CaO	53.80 per cent.
FeO	0.20 per cent.

equivalent to about 98 per cent. calcium carbonate.

Although at one time or another the Shasta Iron Company had planned to make pig iron from this ore, nothing definite was done in regard to the same until the summer of 1906. At that time the possibility of smelting this ore by electricity was brought to the attention of Mr. H. H. Noble, President of the Northern California Power Company, which practically supplies all of the electric power used by the various mines and smelters in Shasta County. After more or less correspondence with Dr. Héroult, plans were made for the erection of a plant, on practically a commercial scale, at a point on the Pitt River. This place was named Heroult.

In July, 1907, the first furnace having been completed, experimental work was begun. This furnace was a 1,500 kw. three-phase furnace of the resistance type. It was soon found that the type of furnace first used presented mechanical difficulties which made its commercial use impracticable, and so it was closed down. Since that time experimental work has been carried on in a 160 kw. furnace, and from the results obtained in this furnace and its method of operation, another 1,500 kw. furnace was designed and built, which at this time would probably be in operation but for the heavy storms of January and February, which caused practically a cessation of construction work during that time.

At present the iron ore is mined by quarrying. From the mine the ore is to be taken to the smelter by means of a surface and gravity tramway. The distance from the mine to the top of the gravity is about 6,000 feet. At the head works at the top of the gravity the ore is to be crushed and dropped into chutes from which it will be released into cars operating on the gravity. The latter is 1,800 feet long and has a grade varying from 15 to 30



Ill. 2.—Section of Furnace and Accessories.

ILL. 2.—Legend.

a—Supply Car.	*g*—Charging Car.	*m*—Bosh and Reducing Stack.
b—Ore Preheater.	*h*—Upper Hopper.	*n*—Contracted Throat.
c—Charcoal Bin.	*i*—Annular Space.	*o*—Melting Crucible.
d—By-Pass Damper.	*j*—Lower Hopper.	*p*—Electrode.
e—Gas Flue.	*k*—Combustion Chamber.	*q*—Electrode Gearing.
f—Gas Stack.	*l*—Air Inlets.	

degrees. On this incline a loaded car going down pulls an empty car up. At the bottom of the incline the loaded car is unhooked from the cable and an empty hooked on. The cars are controlled at the head of the gravity by a worm gear driven by a five horse power motor.

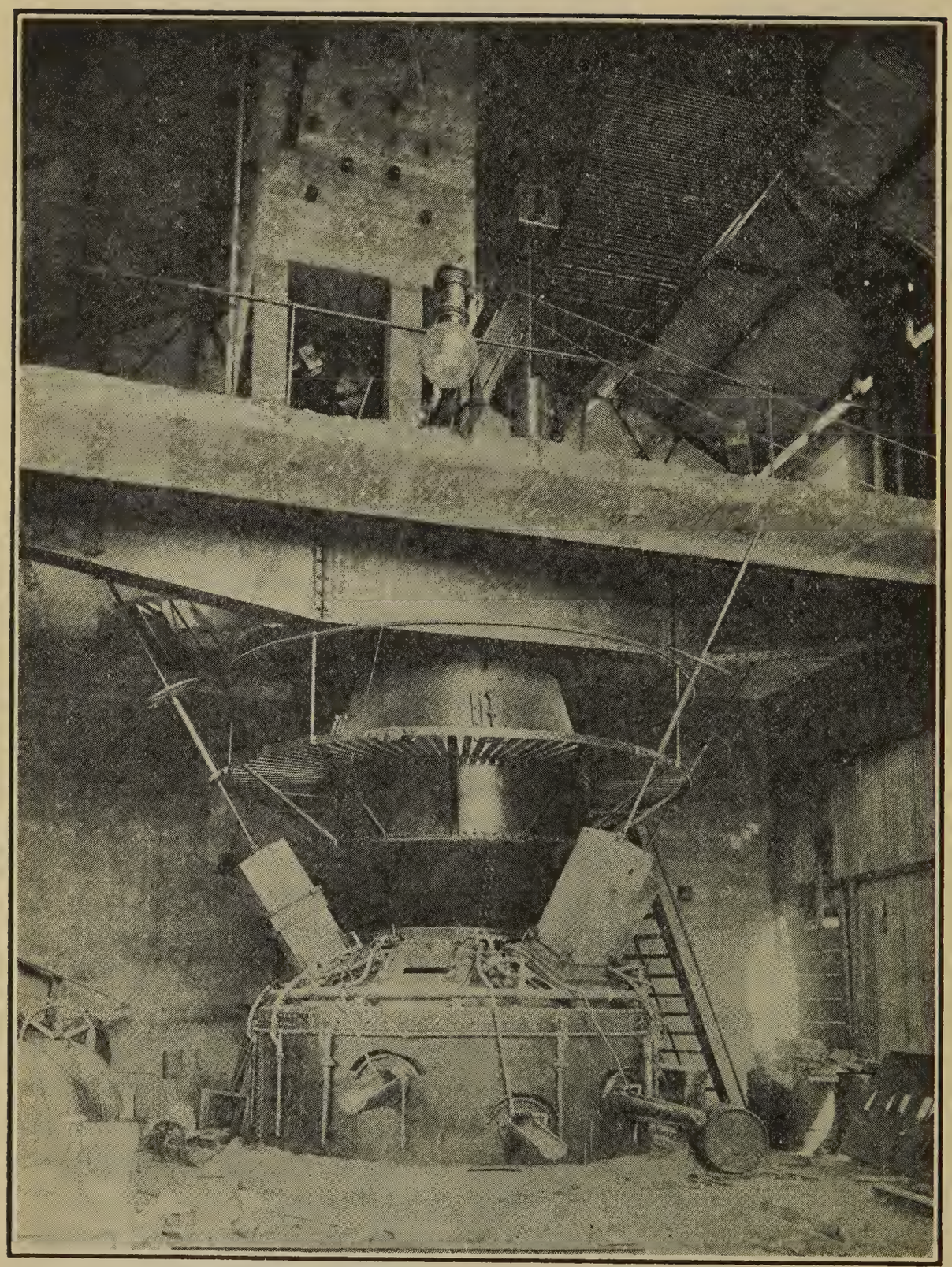
From the bottom of the incline the loaded cars will be trammed to the ore bins, a distance of about 700 feet. From the bins the ore and fluxes will be drawn and transported in hand cars to the furnace building in the supply car (*a*) shown on the following blue print, giving a sectional plan of the furnace room. (Illustration 2).

Referring to the blue print it will be noted that above the crucible at the base of the furnace is a superposed shaft which resembles an ordinary blast furnace and which has a bosh communicating with the crucible.

In the operation of the furnace the ore, mixed with its proper proportion of fluxing materials will be fed into a preheater (*b*) wherein it is to be dried and heated. The source of the heat for the preheater is to be derived from the products of combustion from the combustion chamber (*k*) at the top of the shaft, which will be let into the base of the preheater through a flue (*e*) which communicates with an annular chamber surrounding the top of the shaft and communicating with the chamber (*k*) through openings or ducts (*I*).

A scale car (*g*) runs upon a circular track round the top of the stack and will alternately receive a charge of ore and flux from the preheater (*b*) and a weighed charge of carbon from the carbon hopper (*c*), these charges being delivered alternately by proper mechanism into the body of the furnace.

In the operation of the charging device, a charge of ore and flux will first drop into the upper portion of the hopper, the bell (*h*) being closed, and after the charge is properly distributed about the hopper the bell *(h)* is lowered so as to permit the charge to pass into the lower compartment of the hopper, the



Ill. 3.—View of Furnace in April, 1909.

upper bell being closed and the lower bell (*j*) opened, so as to permit the charge to pass into the shaft. The charge of carbon is then fed into the furnace through the charging device in the same way.

The charge will be kept at about the level of the dotted line shown in the shaft. Above the level are small openings in the shaft with suitable valves for admitting the requisite amount of air to burn the gases resulting from the reduction of the ore in lower part of the stack, thus still further heating the charge, and, as above stated, these waste gases will then pass up through the preheater (*b*) thus preheating and drying the ore before it is charged into the furnace.

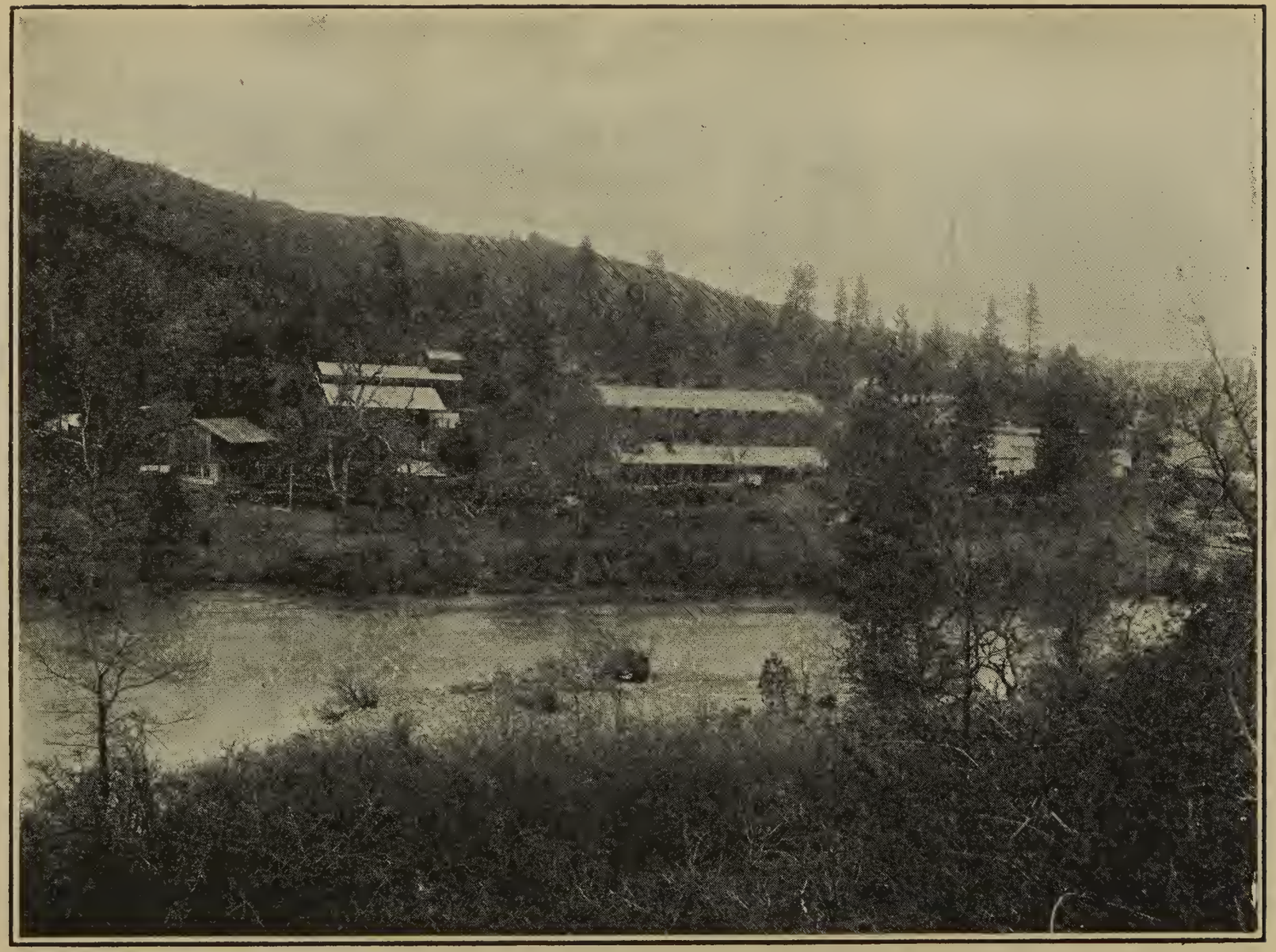
The electrodes, six in number, are so arranged equidistant around the furnace. The electric current passing between them melts the charge and the molten metal and slag are collected in the crucible, from which they are drawn as in ordinary blast furnace work.

Illustration 3 shows the furnace as it exists at the present time. Three of the electrodes are seen in position. Three tap holes are arranged at different levels so that the crucible may be partially or completely emptied as desired. The tap holes are provided with bronze water-cooled casings, as shown in the photograph. No doubt we will make quite a few changes in the next furnace we build, improvements as a result of knowledge gained in the operation of this one.

The electrical equipment consists of three General Electric oil-insulated, water-cooled transformers, having a rated capacity of 750 kw. each, 60 cycles, 2,200 volts primary, and a secondary range of 35 to 75 volts, constant output. The secondary current varies from 10,000 to 21,400 amperes.

The range in voltage is controlled by a dial switch in the primary circuit, giving steps of about 3 volts in the secondary. The efficiency is 98.6 per cent. at 75 volts on the secondary, guaranteed for 25 per cent. overload for 2 hours. The rise in temperature at full load, by test, is 35° C.

The generation of energy in the furnace is therefore controlled externally, without movement of the electrodes, whose position is changed only to accommodate their wear in the crucible of the furnace.



Ill. 4.—Plant Under Construction, From Across the Pitt River.

Illustration 4 is a view of the plant during the period of construction, from across the Pitt River. The buildings prominent in the foreground are part of the plant for making charcoal. Realizing that the cost of charcoal would be an important item, a complete by-product recovery charcoal plant has been installed, under the direction of Mr. W. B. Harper. A standard vertical retorting apparatus, designed to fit our local conditions, has been installed. The equipment consists of eight vertical retorts and four preheaters set in a concrete furnace lined with fire-

Ill. 5.—General View of Plant in March, 1909.

brick; seventeen cages to fit the retorts, each holding two cords of wood; eight tubular condensers, one connected with each retort by means of a copper vapor pipe; several collecting tanks for the condensed vapors; and numerous stills for the refining of the crude products distilled from the wood, such as wood alcohol, tar and acetates. In addition to these essential requirements for distillation of the wood, are the necessary conveyers, pumps, buildings, etc., to make a complete plant.

Illustration 5 shows the plant as it existed at the time of Mr. Bennie's visit, the view looking towards the east.

The following explanatory list is given:

A 25,000 gallon tank.
B Wood storage ground.
C End of tramway.
D Trestle leading from ore bins to charging floor.
E No. 4 Furnace Building, containing 1,500 kw. furnace.
F Charcoal Retort Building.
G Refinery Building.
H Chemical Laboratory.
JJ Bunk Houses.
K Staff and Boarding House.
L Store.
M Retorts.
N Pitt River.
O Ore Bins.

Additional buildings which cannot be seen in this illustration are:

No. 2 Furnace Building, 75 x 35 feet.
Machine Shop and Store Room, 24 x 48 feet.
Office Building, 24 x 56 feet.
Two charcoal kilns of bee-hive form, with capacity of 60 cords each.
Electrical sub-station.

So far our wood for making the charcoal has come by rail. At a point just beyond the retort building (Illustration 5), it is thrown from the car into a conveyer which carries it up along the ridge of a hill and from which it is discharged at any desired point along the line of the conveyer into a small canyon from which it can be trammed out to the retort building as needed.

The retorts are cylindrical in shape and are mounted in an upright position in concrete and brick, there being four retorts to a battery. Each retort holds two cords of wood. The unmounted retorts can be seen in the photograph lying on the wood to the right of the railroad. We are at present putting up two batteries of these retorts. The wood is placed in cages similar in construction to the retorts themselves and these cages then placed in the retorts.

The volatile products obtained during the distillation of wood will be condensed by means of condensers in the building (F)

and then pumped to the refining building (G) where the condensed vapors will be refined into commercial products.

After the distillation of the wood is complete the cage containing the charred wood is to be taken from the retort and placed in a cooling stand until its temperature has been lowered below the ignition point of charcoal.

In the meanwhile another cage containing a charge (two cords) is to be placed in the retort and the charring begun together with the accompanying driving off the volatile constituents. The cages in which the wood is placed are air tight, the opening for the escape of the volatile constituents being closed automatically when the cage is lifted from the retort.

When the charcoal has cooled below its ignition point it is to be discharged into the charcoal storage bin, which is cylindrical and entirely closed except for an opening near the top just large enough to receive the bottom of the cage through which the charcoal is discharged. From the charcoal bin the charcoal is to be taken to the furnace building, hoisted to the charging floor and dumped into the charcoal hopper (*c*) as shown on the blue print. This is the only part of the charge which has to be elevated, the ores and fluxes being handled by gravity.

The wood is converted into charcoal containing about 93 per cent. carbon, the condensable part of the vapors being collected in tubular condensers, the uncondensable gases being led under the furnace and burned. The quality of charcoal that can be made from our wood supply is very good, the following being specimen analyses of charcoal from our ordinary bee-hive ovens:

	I	II	III
Water and volatile matter....	5.3	7.8	6.5
Ash	0.5	0.7	0.6
Fixed Carbon	94.2	91.5	92.9

It is also the intention to introduce at this plant an electrolytic method of making lead acetate, for which there is a certain demand on the Pacific Coast. The entire plant is designed to produce charcoal at low cost for labor, for the utilization of waste heat and saving of time.

At some future meeting of the Society I hope to be able to present a complete paper on the subject, giving in detail the results of my observations on the work we will be doing here.

DISCUSSION.

MR. P. MCN. BENNIE: There is one difference in the method of using gases in the Swedish furnace and the one devised by Prof. Lyon. At *l* there are holes which admit air, and the gases coming from this furnace are burned in an annular chamber, *i*, passing out at *e*, and the iron ore is contained in a double-wall bin around which the gases burn so as to gain some of the heat from the gas, and then is simply charged, in a heated condition, through the bell hopper.

DR. HAANEL: Mr. President, will you permit me to make some remarks in connection with the paper that was read by Mr. Bennie. I have learned a great deal from that paper. I have learned that in making out a report it is always a wise thing to notify the public of your failures as well as your successes. It is as well to know what cannot be done as what can be done. I failed to do that in my report on the experiments at Sault Ste. Marie. I want to supplement that, if you will permit me. The Nobel furnace is constructed, as I understand, with a view of utilizing the carbon monoxide by burning it on top. We made that experiment. We made it over and over again, and we failed for this reason: That the heat generated by the burning of the carbon monoxide is so great that the charge becomes sticky and cannot descend. That is the trouble which they are going to have. They will have to have a number of men poking all the time to get the charge down.

MR. BENNIE: In regard to Dr. Haanel's point that trouble would be found from hanging, it is the intention in this furnace not to have the charge higher than is shown by the irregular lines. From the previous experiments it is believed that no trouble will result; that the gas will always be burning above the charge, air being introduced at L and burned in the annular chamber, I.

PROF. JOSEPH W. RICHARDS: Mr. Chairman, the question of the particular suitability of electric furnace pig iron for making steel is, I think, an important point that is worth discussing. The question is whether pig iron made in the electric furnace, without the use of atmos-

pheric air, will be any different in its characteristics from pig iron made by the use of blast. The results of Braun, in Sweden, analyzing pig iron, have not been confirmed, but they indicated that nitrogen was present in pig iron as obtained from the furnace, and that steel made from that pig iron did not lose all its nitrogen in the process of manufacture; that there was less nitrogen in Bessemer steel than in the pig iron from which it was made; there was less in open hearth steel than in the Bessemer steel, and there was less in crucible steel than in open hearth steel, and that possibly the nitrogen is the cause of the inferiority of open hearth steel to crucible steel, or one of the causes. Now, I should very much like to see somebody make steel from electric furnace pig iron by the Bessemer process, the open hearth process and the crucible process, have the work carefully checked, and see whether there is not a steel obtained different from ordinary steel, which may possess characteristics of its own because of the absence of some ingredient like nitrogen, which is present in blast furnace pig iron and not in electric furnace pig iron.

DR. R. MOLDENKE: Has any test been made to determine the presence of dissolved oxides in the pig iron? We foundry men are very much interested in the question of the quality of electric furnace pig iron as compared with that made ordinarily in the blast furnace. From a personal experience in the production of over 225,000 tons of castings I have come to the conclusion that the difference between good and bad irons of apparently the same compositions is simply their content in oxygen. I have made iron in the open hearth furnace for malleable castings which was so badly burned in the melting that it could hardly be poured from the ladle, and yet it contained only 0.03 oxygen, in the shape of dissolved oxides of iron. If electrically made pig iron is going to be freer from this trouble than what we get now, I predict a great future for it in the specialty shop, where the best quality of metal is essential.

PROF. RICHARDS: To my own knowledge such analyses of pig iron made from the electric furnace as would set that point at rest have not been made. I wish that they could be made.

A paper presented at the Fifteenth General Meeting of the American Electrochemical Society, at Niagara Falls, Canada, May 6, 1909, President E. G. Acheson in the Chair.

THE ELECTRIC FURNACE REDUCTION OF IRON ORE

By Joseph W. Richards.

In order that one can understand thoroughly the problems arising in the reduction of iron ore by carbon in an electrically heated furnace, he should first of all have a clear idea of how this reduction proceeds in a ordinary, non electrical blast furnace.

Blast Furnace Practice.

The iron ore contains iron oxide, with silica and clay as usual impurities, and more or less moisture; its phosphorus content may be low or high, but its sulphur content must be low, not over 0.5 per cent. If the ore carries over 1 per cent. of sulphur it is given a preliminary roasting. In the furnace perhaps 99 per cent. of the iron oxide is reduced to metallic iron, 10 to 20 per cent. of the silica is reduced by carbon to silicon, which combines with the iron, all of the phosphorus is reduced into the pig iron, and a varying proportion of the sulphur, this proportion being smaller the more basic the slag is made with lime and the higher the running temperature.

Flux is added to make fusible slag by combining with the unreduced silica and the clay in the ore. Limestone, unburnt, is the usual flux, but magnesian limestone, carrying $MgCO_3$, is quite commonly used, the magnesia increasing the fusibility of the slag if not in greater proportion to the lime than the proportions 2CaO.MgO. The amount of flux added is variable, it depends on how basic the slag must be made. If the fuel is coke, and therefore considerable sulphur comes into the furnace, the slag formed must be nearly half lime and magnesia, to make low sulphur pig iron; if the fuel is charcoal, carrying almost no sulphur, and the ores carry none, the slag may be only one-third lime and magnesia and two-thirds silica and alumina, and make

best quality pig iron. Such slag costs less for flux and is more fusible than the basic lime slags.

Fuel is needed to provide heat and reducing effect. The heating effect is almost entirely produced by the combustion of the larger part of the fixed carbon (non-volatile carbon) of the fuel to carbon monoxide (CO) before the tuyères. This combustion fills two functions: It provides the high temperature necessary to melt down the iron and slag, and it provides large quantities of reducing gas, practically identical in composition with producer gas (30 to 35 per cent. CO, 1 to 2 per cent. H_2, rest N_2), which does in the upper part of the furnace the larger part of the reduction performed in the furnace.

The amount of fuel used in a blast furnace is determined by the amount which must be burned at the tuyères to produce the necessary smelting temperature, and not by the amount necessary to perform the reduction of the metallic oxides. The amount necessary for performing the reductions taking place in the furnace is only one-third to one-half of the amount necessary to be burned to provide the smelting heat. That this statement is true of the ordinary blast furnace may be seen from the fact that if the smelting zone is increased in temperature by heating the blast, the amount of carbon used in the furnace per unit of pig iron made is at once decreased. Or, if the heat available in the smelting zone is increased by drying the blast, and thus removing the strong cooling influence which the decomposition of the moisture of the blast exerts, economy of fuel at once results. In fact, any means of getting high smelting temperature without combustion of carbon before the tuyères, decreases at once the quantity of fuel necessary to use in the furnace, since the quantity used is determined by the heat requirements in the smelting zone and not by the requirements for reduction, which are only a fraction of the former.

The ash of the fuel is largely silica, with some alumina and lime, if coke, or alkalies, if it is charcoal. This requires flux to slag it, an amount which may be considerable when using poor coke high in ash. Regard for this item of cost should be had in purchasing or valuing the fuel.

The pig iron produced contains carbon between 2.5 and 4.5 per cent., silicon in varying quantity, 1 to 4 per cent., according

to the temperature and rate of running of the furnace, practically all the phosphorus of the charge, and one-tenth to one-fourth of the sulphur. Its melting point is about 1200° C., and it runs from the furnace ordinarily at 1500° to 1600° C., carrying out as sensible heat 250 to 300 calories.

The slag may be basic or acid, as before explained, and these varieties will average in per cents.:

	Basic Slag High Sulphur Charge	Acid Slag Low Sulphur Charge
SiO_2	35	55
Al_2O_3	10	10
CaO	40	25
MgO	10	5

These slags melt at about 1350° and 1200° C. respectively, and ordinarily run away from the furnace at 1600° C., carrying out as sensible heat 500 calories.

The reduction of silica and phosphorus oxide in the furnace is accomplished by solid carbon in the smelting zone. A small part (10 to 20 per cent.) of the iron oxide in the furnace is also similarly reduced by fixed carbon; the rest is reduced in the upper half of the furnace by the excess of carbon monoxide gas. So much of the latter gas, however, is produced before the tuyères in generating the temperature necessary in the smelting zone, that only a fraction of it is converted into carbon dioxide, CO_2, in reducing the iron oxides of the charge. This is the chief reason for the excess of unused carbon monoxide in the gases of the blast furnace, an amount whose potential calorific value often represents one-half of the calorific power of the fuel put into the furnace. It is true that all the carbon monoxide in the gases could not be utilized no matter how small its amount, but that is a limit set by the principle of chemical equilibrium or mass action, which ordinarily is not approached because of the excessive amount of carbon monoxide produced in the lower part of the furnace in the effort to get the requisite smelting heat and temperature. The proportions of carbon ordinarily consumed at the tuyeres are 9 atoms (108 parts) of carbon for each molecule of iron oxide (160 parts) reduced by the carbon monoxide gas. The chemical equation is:

$$Fe_2O_3 + 9CO = 2Fe + 3CO_2 + 6CO.$$

This equation shows us that only one-third of the carbon monoxide produced before the tuyères, in generating the smelting temperature, is utilized in reduction, while two-thirds escapes unused.

Electric Smelting Furnace.

Passing to the electric principle of smelting, we have here to deal with the case of all necessary heat supplied by electrical energy, no blast blown in, and therefore all the solid carbon utilized for reduction (always excepting the small amount which dissolves in the pig iron). In calculating the amount of carbon necessary to thus reduce the iron oxide, we meet at the outset with this difficulty: What proportion of the carbon will form CO_2 and what proportion CO? We know that when reduction takes place at a very high temperature, CO is almost the only product; but as this passes more or less slowly through the cooler portions of unreduced charge, CO_2 is formed in increasing amounts, until at a low red heat, given sufficient time, about half the CO may be converted into CO_2. The formulas corresponding to these two extremes are:

$$Fe_2O_3 + 3C = Fe_2 + 3CO.$$
$$Fe_2O_3 + 2C = Fe_2 + CO + CO_2.$$

Comparing these with the ordinary blast furnace reaction, which requires 9C put into the furnace for the reduction of Fe_2O_3, we see that 3C, or one-third as much carbon, is the greatest amount necessary in the electric furnace reduction, and 2C, or between one-third and one-fifth as much, is the smallest amount necessary. As will be further shown, the uncertainty as to how much CO_2 can be formed in the electric furnace reduction is perhaps the chief difficulty in running the electric furnace.

Example: Iron ore is to be reduced to pig iron in an electric furnace, and the flux and charcoal on hand for the charge analyze as follows:

Iron Ore		Limestone		Charcoal	
Fe^2O^3	90	$CaCo^3$	90	Fixed C	90
SiO^2	8	$MgCO^3$	8	Volatile Mt'r	6
Al^2O^3	2	SiO^2	2	SiO^2	2
				Al^2O^3	1
				K^2O, Na^2O	1

Assume the pig iron made will contain 4 per cent. of carbon and 3 per cent. of silicon; that the slag may be 65 per cent. SiO_2 plus Al_2O_3; that the gases contain only the CO_2 from the limestone, and none from the reductions.

Required: (1) The weights of ore, limestone and charcoal to charge per 100 of pig iron made. (2) The percentage composition of the gases. (3) The weight and percentage composition of the slag.

Solution: (1) The weight of ore needed is that necessary to supply the 93 parts (100-4-3) of iron in the pig iron. This will require $93 \times \frac{}{} = 133$ parts of Fe_2O_3, which will be contained in $133 \div 0.90 = 148$ parts of ore.

The weight of charcoal needed is that necessary to furnish enough fixed carbon to reduce the iron oxide and that silica which is reduced, and to supply the carbon in the pig iron. These quantities are:

Reduction of Fe^2O^3 : $93 \times \frac{36}{112}$	= 29.9
Reduction of SiO^2 : $3 \times \frac{24}{28}$	= 2.6
For carbon dissolved :	= 4.0
Total requirement	= 36.5
Charcoal required $\frac{36.5}{0.90}$	= 40.6

The weight of flux required is best found by calling it x, and then figuring out the slag, as follows:

Silica in the slag will be that in the ore, flux and fuel, minus that reduced to silicon. Therefore,

In ore	148	× 0.08	= 11.8
" flux	x	× 0.02	= 0.02 x
" fuel	40.6	× 0.02	= 0.8
Reduced	3	× $\frac{60}{28}$	= 6.4
Silica in slag			= 6.2 + 0.02 x

By similar calculations we find the slag to contain, as a whole:

Silica	6.2	+ 0.02 x
Alumina	3.4	
Lime		0.50 x
Magnesia		0.04 x
Alkalies	0.4	
Total weight	10.0	+ 0.56 x

If the slag is to be 65 per cent. of silica and alumina together, then

$$0.65(10.0 + 0.65x) = 9.6 + 0.02x$$

from which $$x = 9.$$

The above solution is perfectly general, and applies to all kinds of ore, flux and fuel, and the production of any desired kind of slag.

(2) The gases will contain the fixed carbon of the charcoal (except that part which goes into the pig iron) in the state of CO, the carbonic acid driven off the flux, and the volatile matter from the charcoal. The latter may be assumed as composed of equal parts by volume of hydrogen, carbon monoxide, and carbon dioxide, which would correspond to weights of those gases in the proportion of 2:28:44. The gases passing off will therefore be, in parts by weight:

CO from fixed carbon	: 32.5 × $\frac{28}{12}$ = 75.8	} 76.8
CO from volatile matter	: 2.7 × $\frac{28}{44}$ = 1.0	
CO^2 from volatile matter	: 2.7 × $\frac{44}{44}$ = 1.6	} 5.6
CO^2 from flux	: 9.0 × 0.44 = 4.0	
H^2 from volatile matter	: 2.7 × $\frac{2}{44}$ = 0.1	0.1
Total weight of gases		82.5

Percentage composition of gases by volume:

CO	76.8 ÷ 1.26	= 61.0	= 94.0%
CO^2	5.6 ÷ 1.98	= 2.8	= 4.3%
H^2	0.1 ÷ 0.09	= 1.1	= 1.7%
		64.9	100.0%

The volumes 61.0, 2.8 and 1.1 represent cubic meters of these gases per 100 kilograms of pig iron made; if multiplied by 16 they give the cubic feet per 100 lbs. of pig iron.

(3) The slag will contain, substituting $x = 9$:

Silica	6.4 =	42.4 %
Alumina	3.4 =	22.5 %
Lime	4.5 =	29.8 %
Magnesia	0.4 =	2.65%
Alkalies	0.4 =	2.65%
	15.1	100.00%

CHARGE SHEET—Per 100 of Pig Iron Produced

Charges		Pig Iron		Slag		Gases	
Ore:	(148.0)						
Fe^2O^3	133.2	Fe	93.0			O	40.2
SiO^2	11.8	Si	3.0	SiO^2	5.4	O	3.4
Al^2O^8	3.0			Al^2O^3	3.0		
Limestone:	(9.0)						
CaO	4.5			CaO	4.5		
MgO	0.4			MgO	0.4		
SiO^2	0.2			SiO^2	0.2		
CO^2	4.0					CO^2	4.0
Charcoal:	(40.6)						
Fx'd C	36.5	C	4.0			C	32.5
CO	1.0					CO	1.0
CO^2	1.6					CO^2	1.6
H^2	0.1					H^2	0.1
SiO^2	0.8			SiO^2	0.8		
Al^2O^3	0.4			Al^2O^3	0.4		
$(NaK)^2O$	0.4			$(NaK)^2O$	0.4		
Totals	197.9		100.0		15.1		82.8

COMBINED BLAST AND ELECTRICAL FURNACE.

The electrical reduction of iron ore differs radically from blast furnace practice in one essential particular, *viz.*, that since no air is blown in, any excess of carbon above that consumed in reduction must remain unused, accumulate, and eventually clog the furnace. The amount to be used as a minimum cannot, moreover, be calculated until we know how much CO_2 will be formed in reduction, and that is an unknown quantity unless arrangements are made so that none can be formed. The following modifications of working an electrical pig iron furnace are possible, with the object in view of avoiding the accumulation of excess carbon in the crucible.

(1) A deficit of carbon may be put into the charge, thus permitting unreduced iron oxide to escape in the slag, and preventing unused carbon from accumulating. This solution leads to the disadvantages of loss of iron, heavy corrosion of lining of furnace, and heavy consumption of electrode carbon. It may have the secondary result of preventing reduction of silica or taking up of carbon by the iron, and thus furnish a metal with high melting point and approaching steel in composition. Such

slag would also remove some of the phosphorus in the charge, but practically no sulphur.

(2) A charge of ore and flux without fuel may be run through the furnace whenever an accumulation of carbon occurs, as is shown by the resistance of the furnace falling off and the furnace getting cold. This was the device adopted in the experiments of the Canadian commission at Sault Ste. Marie, but while permissible in experimental work, it would not do to thus periodically derange a furnace in regular running.

(3) The fuel may be calculated only for the production of CO in the furnace, and this condition approximated by leading off the gases from the hot part of the furnace and not allowing them to cool in contact with the ore. In this way reduction by CO is avoided, and the fixed carbon in the charge may be consumed almost entirely to CO without formation of CO_2. This would bring the furnace consumption of carbon nearer to a definite amount, and by avoiding reduction except by solid carbon tend to use up all the carbon charged, the amount of which would be calculated by this manner of working (as in the numerical example worked out for illustration).

(4) The best solution of this difficulty may be to provide tuyères by which air can be sent into the crucible of the furnace, and thus burn any accumulation of carbon. A given quantity of air will always burn a given quantity of carbon, and therefore the cure would seem to lie in having a *variable* supply of air, which is increased whenever the falling resistance of the furnace indicates that carbon is beginning to accumulate, and diminished to a small minimum supply, only enough to keep the tuyères open, when the furnace is in good electrical running order. It would represent a combined electrical and blast furnace, with the blast so regulated as to overcome the chief difficulty of the purely electrical furnace—the accumulation of unused carbon in the crucible.

It may be quite possible, by some such device as Mr. Taylor's large electrical furnace, to practically combine the blast furnace and the electrical furnace. The writer is quite confident that any practicable method of introducing electrical heat into the crucible of a blast furnace will result in large economies in the furnace working. Only one-quarter of the heating power of the fuel is

developed around the blast tuyères, and yet if half of this could be replaced by electrically generated heat, an economy of 50 per cent. could in all probability be reached upon the fuel bill. To put it into figures, it takes 1.2 tons of coke to make a ton of pig iron in the blast furnace, and about three-quarters of a ton is burnt by the blast, producing at the smelting zone about 25 per cent. of the calorific power of the coke. If electrical energy could be made to supply only one-half of this, the furnace would make iron with half the previous coke supply, that is, with 0.6 ton of coke per ton of pig iron, and this with an expenditure of electrical energy equal only to 12.5 per cent. of the calorific power of the coke, that is, equal to the calorific power of but 0.15 tons of coke.

The question of economy in this case will not be, then, the simple replacement of fuel heat energy by an equivalent amount of electrical heat energy, but the comparison of fuel heat energy with the cost of *one-fourth* its amount of electrical heat energy. This may be quite possible in many localities, and the combined furnace would work more regularly than a purely electrical furnace. The question awaits the coming of the electrometallurgical engineer who can make practicable the requisite combination. A possible solution may be to use cheap electrical power to super-heat the hot blast, and thus to make the blast itself the agent for carrying electrically developed heat into the furnace.

Metallurgical Laboratory,
Lehigh University,
April 7, 1909.

A paper read in abstract by Jos. W. Richards, at the Fifteenth General Meeting of the American Electrochemical Society, at Niagara Falls, Canada, May 6, 1909; President E. G. Acheson in the Chair.

THE APPLICATION OF THE ELECTRIC FURNACE TO SIDERURGY.

By Major Cav. Ernesto Stassano.
Director of Forni Elettrici Stassano, Turin, Italy.

(Translated by F. A. J. FitzGerald.)

PART I.

There are few problems which, having been neglected for a certain time, have so quickly and profoundly attracted the attention of the technical world as the application of the electric furnace to the metallurgy of iron and steel.

This fact, which is interesting to everyone, is still more interesting to me, who was one of the first to study the problem and try to find a practical solution of it. I consider this a recompense and a reward for a great many years of hard work.

Having been invited by the American Electrochemical Society to give an account of the study I have made in this direction, and appreciating the honor shown me, I compiled the following in order to demonstrate the result of my researches and experiments, and I shall be glad if this testimony of my good will may be of some use to those who generously favored me with this invitation.

Side by side with the interest of technical persons in this subject there is a strong current of competition among those who have worked in this field and, though this competition seems perfectly natural up to a certain point, seeing that the question is closely connected with one of the most important branches of industry and attracting great public interest, yet whoever undertakes to deal with the subject must point out clearly in an impartial manner the fundamental basis of this most important problem of electrosiderurgy before showing the practical results which have been obtained. It appears to me

that this is the only way in which those interested in the subject can appreciate the results, for these must be freed from the exaggerations and inexactness which characterize a general competition.

Hence, following the advice of the promoters of the meeting, I must premise certain considerations of a general kind before explaining the practical results I have obtained.

The electric furnace, taken in the most simple meaning of the term, is nothing but an apparatus for transforming electric power into heat to be used in metallurgical operations. All that the electricity supplied to such an apparatus has to do is to transform its energy into heat in a practical and convenient way.

In the present state of science such a transformation may be performed either by passing the current through the material which, if a conductor of electricity, will thereby be heated. Or the current may pass through the air by means of two carbon electrodes placed quite near to the material which, in this case, belongs to the class of non-conductors.

In either case the transformation of energy follows Joule's law, viz.: The work of the current in overcoming the resistance of either solid material or the air.

Passing through the air, the current, in order to complete its circuit, forms an arc, thus producing a very high and constant temperature, which is quite independent of the amount of the current. On the other hand, when passing through a conducting metal or the like in a furnace, the quantity of energy, and, in consequence, the temperature developed, is function of the quantity of electricity employed and of the resistance of the conductor. The resistance of the conductor is determined by its resistivity, its length and its cross-section.

If, however, the electric energy which is to be converted into heat is furnished in the form of alternating current, it is possible to heat the material, according to Joule's law, provided the material is a conductor, without closing the circuit on the material itself. This can be done if the material is so arranged as to form the secondary circuit of an ordinary transformer.

Although there is only one way of transforming electrical energy into heat, the apparatus for bringing about this transformation are of three kinds:

(1) Apparatus for the treatment of materials in which the latter are connected to the terminals of a generator. This I shall call "resistance furnace."

(2) Apparatus in which the current passes from one electrode to another in the form of an arc which heats either by radiation or by direct contact, the metal to be melted until the latter is liquified. These, I shall call "arc apparatus."

(3) Apparatus in which heat is generated in the mass of metal by induced currents, the metal being arranged so as to form the secondary circuit of a transformer. These, I shall call "induction furnaces."

The fundamental principles of these three types which are in actual use are not new.

In fact, in the first practical application, it was designed to heat and melt metallic iron by passing a current through it. The first practical application may be found in the well-known fuse used in electric circuits. This may be considered the starting point of what I called "the resistance furnace."

For the sake of research and not for industrial purposes, scientific men made use of the heat produced by the electric arc, to melt metals, adapting various contrivances for identical purposes. Thus, in 1879, Siemens was successful in solving the problem with his famous electric crucible furnace, and the small furnace heated by radiation from an arc between two horizontal electrodes was afterwards used by Moissan in his well-known experiments, thus giving a more complete solution of the problem. These are the early types of the present electric arc furnaces.

An English electrical engineer, Mr. Ferranti, in 1885 foresaw the possibility of using induction by a magnetic circuit, as may be observed in every static transformer, to heat and melt metals. The metals were arranged like the secondary of a short circuited transformer. Thus he gave a hint for the construction of the "induction furnace."

Before these ideas became of practical use in the industry a long time had to pass. Then we reach the invention of Cowles for the production of aluminum alloys in 1886, and then the Willson furnaces for the manufacture of calcium carbide in 1892, and the apparatus for the production of metallic alloys and metallic

carbides based on the transformation of electric energy into heat.

It is not my purpose to enter into the history of the electric furnace and, therefore, I come directly to the examination of furnaces such as are actually used in industry and especially in the metallurgy of iron and steel. Moreover, I shall confine myself to those inventions which have actually been used and for this reason only, have interest for the industry. Conforming to the above specifications I may arrange them in five classes.

(1) The resistance furnace in which the current is conveyed directly to the material to be heated by means of solid contacts, the latter being conductors. This type has been used practically by Dr. Acheson for the manufacture of artificial graphite.

(2) Arc furnaces based on the principle of Siemens' crucible furnace where the electric current is led from an electrode through the material and passes out through the conducting bottom of the hearth to the other terminal of the generator. In practice this type is used for the production of calcium and metallic carbides, and has been especially adapted for the manufacture of pig iron by Dr. Héroult and for the refining of iron and steel and the melting of iron ores by Mr. Keller.

(3) Arc furnaces in which the electric current going from one electrode through the conducting material returns by an arc to the other electrode, connected to the remaining terminal of the generator. This type is largely used for producing molten calcium carbide, and has been adopted by Dr. Heroult for the production of iron and steel.

(4) Arc furnaces based on the small Siemens furnace where the arc plays between two carbon electrodes quite independent of the materials to be treated and heating the latter by radiation. It is to this class that my furnaces belong, and they allow the production in a single operation of malleable material directly from iron ore, as well as the melting and refining of iron and steel.

(5) Induction furnaces where the current to be changed into heat is transformed by electric magnetic induction into a current passing through the metallic mass to be melted. This metallic mass forming the secondary of a static transformer. This type of furnace, based on the work of Ferranti, has been developed by Dr. Kjellin and others.

I will omit a detailed description of these furnaces as they are well known, but before proceeding to the examination of the results which have already been obtained, or may be obtained in the future, I think it necessary to mention two facts of great importance in view of what I have stated above, viz:

(1) In the different types of electric furnace actually in use, the electric energy supplied to them has no special action beyond that of its practical and convenient transformation into heat. Since this transformation is always performed in the same manner, the furnaces from the point of view of metallurgy have to be considered like ordinary furnaces.

If this particular method of generating heat gives advantages which ordinary furnaces using coal or other fuel do not possess, that does not mean that these advantages or merits are a peculiarity of any one of the above mentioned furnaces.

(2) None of the furnaces in use are based upon principles which were unknown at the time of their appearance and consequently their technical and commercial value are determined by the details of construction insofar as these contribute to the better utilization of this new source of heat.

Now let us consider the results obtained with the electric furnace. The first application of this apparatus and that to which is due its development in the industry, is doubtless its use in the manufacture of calcium carbide. Therefore, I think it is necessary to examine this use before studying its application in the electro-metallurgy of iron and steel.

As is well known, this material is produced by the reduction of calcium oxide with an excess of carbon. The latter combines with the oxygen of the lime and gives in exchange two atoms of carbon required for the formation of the carbide. Lime, the most refractory of oxides, which the heat developed by an oxy-hydrogen flame neither melts nor reduces, can only be acted on by the heat of an electric arc, which produces the highest temperature that can be obtained.

The furnaces designed by Willson and later improved by Bullier, were only reproductions of Siemens' crucible on an industrial scale, for they consisted of a conducting bottom upon which lime and carbon were placed, also of an electrode which being at first placed close to the conducting bottom was eventually with-

drawn forming an arc, the heat of which caused the reduction of the lime and consequently the formation of carbide. The latter substance becoming a conductor at the high temperature of the reaction, then performed the function of the conducting bottom, conveying the current which passed from the electrode in the form of an arc and thus leading to the production of more carbide.

With further progress in the industry, it was found that the carbide which was originally crystallized became molten with the increased temperature and in this form had certain advantages. This brought out the disadvantage of the conducting bottom. Then two vertical, parallel electrodes were adjusted to the furnace, each electrode being connected to a terminal of the generator. These electrodes each formed an arc on the bottom of the furnace and afterwards on the charge which became a conductor and remained so till the carbide was liquified.

Owing to the fact that large quantities of carbon monoxide are developed during reaction and, owing to the fact that lime, the chief component of the carbide is a non-conductor of electricity at low temperature so that the electrodes may be plunged in the same without any risk and finally considering that the lime mixture covers the already fluid carbide and prevents loss of heat around the arcs by radiation, it was possible to build the furnaces without any covers. But in treating certain other carbides and certain less refractory metals the case is different.

When, in 1896, I was interested in the manufacture of calcium carbide and conceived the idea of applying this new and powerful source of heat found in the electric furnace to the reduction of iron ore and to siderurgy in general, I discovered that for this purpose the furnace should not be built on the principles mentioned above, and for that reason gave the preference to the type of recuperative furnace with horizontal electrodes proposed by Siemens. Let us consider the following points:

(1) Heat developed without fuel from the new source does not require air circulating in the melting chamber.

(2) Iron ore and materials containing iron are conductors of electricity, and hence electrodes cannot be plunged in the materials to be treated. Therefore, the arc cannot be concentrated

upon the bath and the loss of heat avoided as in the case of the carbide furnaces.

(3) Iron unlike lime, does not produce a definite carbide, but many kinds of carbides having different contents of carbon.

(4) Neither iron ore nor iron are so refractory as to require the heat of the arc itself in order to become molten.

(5) It is likewise obvious that an electric furnace to treat iron ore and iron for the production of a suitable grade of steel directly from the ore cannot be constructed like a calcium carbide furnace.

Pursuing my study, I discovered the requirements necessary for this application of the new heat generator. Such qualities, I will point out in the most simple manner, because they are self-evident and it is useless to repeat what I have demonstrated elsewhere.

(1) The vessel in which the energy is to be converted into heat should be hermetically closed so that a neutral atmosphere, chemically speaking, is maintained.

(2) The heat developed has to be generated at the highest temperature possible.

(3) No foreign substance may be brought into contact with the charge if it is desired to avoid its pernicious effect on the composition of the latter.

(4) The apparatus to carry out the metallurgical operation by aid of electric heat and the process associated therewith should be designed so as always to work with a full charge.

Beginning with the study of an electric furnace for the reduction of ore and the refining of pig iron and iron bearing materials in general, I have endeavored as far as possible to base it on the principles mentioned above and stopped at the rotary type which has been described in all the leading periodicals, so that without any prejudice to the clearness of the present paper I may dispense with commenting thereon.

Now let us examine the different types of furnace actually in use and it will be readily seen that my system is answering as far as is practically possible all requirements of this new and powerful source of heat, while other systems adjust themselves only partially to the four fundamental principles. Indeed omitting the resistance furnace which has no application at all in

electrothermic metallurgy we have to comment only upon the remaining four types.

(a) My furnaces comply thoroughly with the first of the requirements. The electrodes held in metallic clamps are fitted in the casing of the furnace so that no air can pass between them and the charging door through the melting chamber. The melting chamber is thus hermetically closed, while in furnaces where two distinct arcs are in circuit with a conducting bottom which forms one terminal of the circuit, it is impossible to avoid the entrance of air which destroys the neutrality of the atmosphere in the melting chamber, and has a disturbing influence on the arcs. The arcs in these furnaces can never attain the length nor reach the stability they have in my furnaces where they may be considered as enclosed arcs.

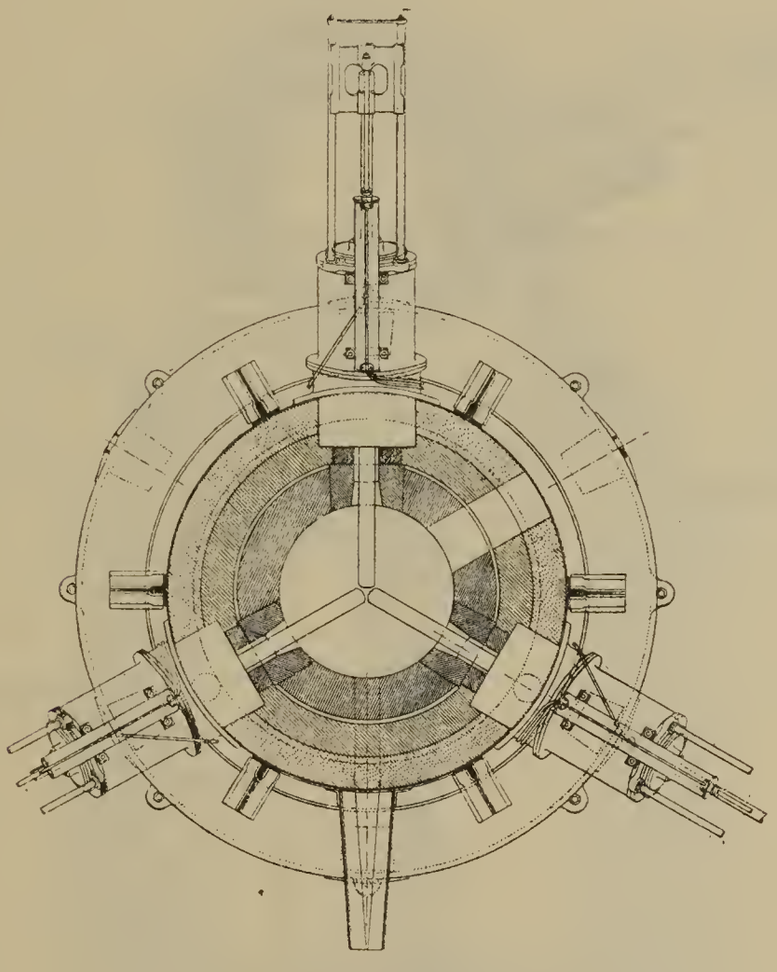
In the induction furnace it is difficult to close perfectly the channel which forms the melting chamber and this because of electrical reasons. In this furnace there is not a neutral, but rather a slightly oxydizing atmosphere.

(b) The second requirement with which in general arc furnaces should comply is not fulfilled by the induction furnace, because in these the temperature is the result of the quantity of current employed and the resistance of the bath. Besides this, curious phenomena which have not yet been explained, appear in the molten mass.

(c) The third requirement which is fully complied with both the induction furnace and by mine is only partly complied with in the other arc systems. This is shown by the fact that while in my furnace (in which also non-conducting materials can be treated) malleable iron may be produced directly from the ore and in a single operation, and, while either in my furnace or in those of the induction type, iron and steel may be refined without the use of a big mass of slag on the bath, the same cannot be done in any other furnace, where starting with ore only cast or pig iron will be obtained. It is impossible to refine without placing a thick layer of slag on the bath between the electrodes to protect the metal against the action of the carbon of the electrodes and against the action of the oxygen of the air.

(d) In my furnace materials can be thoroughly mixed by agitation, which increases the activity of the reaction producing

the refinement and shortens the time, thus making possible work on a full charge without risk of over-heating the chamber or damaging the lining. The advocates of other systems than mine deny the importance of mechanical motion, pretending that a difference of temperature existing in various parts of the bath causes a circulation in the molten mass and that this is quite sufficient to stimulate the refining action. Admitting this kind of motion, if it really exists, then it must likewise occur in my system. And this proves that the criticism is without founda-



tion, for there is no doubt that improved results are obtained by agitating the molten mass, using a two-fold motion, the natural and the mechanical.

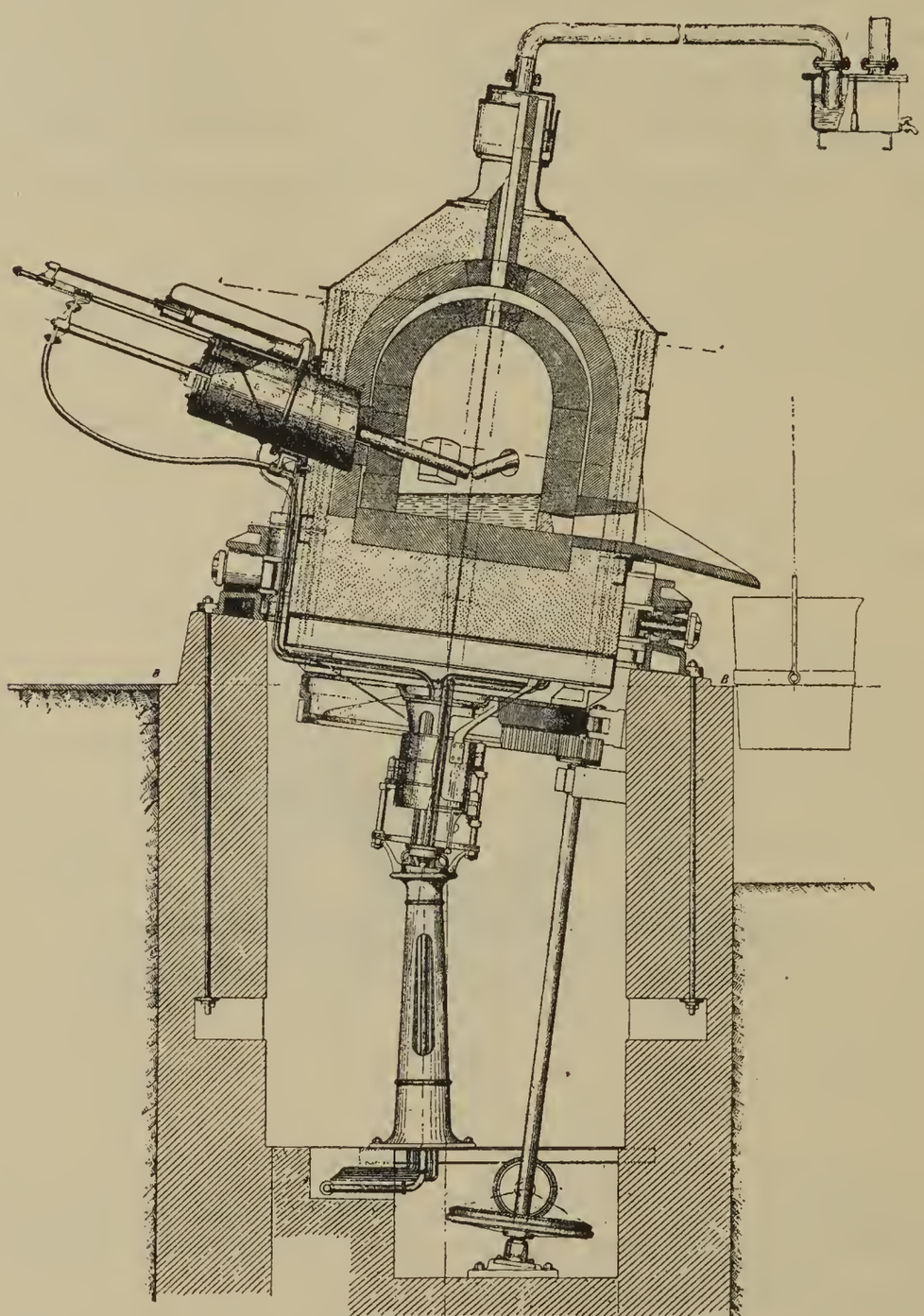
This is not the only criticism against my furnaces, others have been brought forward, especially by persons who never saw one of my furnaces working. Considering the matter more closely I find that it is said:

(1) That my furnaces are complicated.

(2) That the arrangement of the arcs is such as not to heat

the metal sufficiently and hence that no high grade refining can be done.

(3) That the refractory lining is submitted to more serious wear and is consequently more costly.



Is there any reason for these criticisms?

Frankly speaking, I may say "No," and I shall prove this later on. However, before entering into this matter I beg leave to add a few words of a non-technical character.

To one of the articles criticising my furnaces, I headed my

answer with the Latin phrase "Ne quid expectes amicos, quod tu per te agere possis." (Do not expect from friends what you can do yourself)—a quotation which I took not for the purpose of showing my erudition, but because I believe that all who spend their time, labor and money in the study of this important problem of electro-thermic metallurgy should publish the results of their work, and make use of their right to defend it like I did and always will do without the aid of friends more or less interested, and that under such circumstances no unfair criticism would have made its appearance. Sometimes criticism has transgressed the limit, leaving a serious basis, and not infrequently abandoning the truth. This, of course, gave a hostile turn to the discussion and made it useless, while, if properly carried on, it would have been a great help to the development of a question which interests the whole world.

I beg your pardon for this digression and will now continue on the proper subject.

An experience of several years with my furnace obtained by people who had no interest at all in taking them up if they did not give satisfactory results, proves sufficiently that none of the three faults mentioned above, and particularly attributed to my system, do exist, and speaking to a meeting of technical people, it is my duty to demonstrate the correctness of my assertion. After examination of the details of my furnaces, it is easy to see that there is no complication, or that the complication is not greater than in other systems.

In the present state of the industry, the regulation of electrodes by means of a simple, trustworthy and convenient device such as hydraulic rams, which I have adopted, is not in any way a complication, nor can it be said that it is more complicated than gears, spur-wheels and similar devices which characterize the automatic governors of other arc furnaces. In other arc furnaces the current density in the electrodes is low, not over four to five amperes per square centimeter, and the low power factor necessitates the use of electrodes having far greater dimensions than mine. The smallest of my furnaces can be used with a current of one hundred and twenty volts and current density in the electrodes of twenty amperes per square centimeter.

The casings I use to protect the electrodes which are inserted

with air-tight joints in the cover and cooled by means of a water jacket are not open to criticism.

(1) Water jackets are used in other kinds of arc furnaces and if they are considered complicated, it is one common to all and hence no blame can be laid on me.

(2) The advantage of this is far superior to the inconvenience which is only apparent. With my design I have an apparatus which is perfectly air-tight, and thus secures perfect neutrality in the chemical sense of the word. The high current density in my electrodes is certainly an economical factor.

The only things then which remain for discussion are the mechanical movement of the furnace, the sliding contact of the collector rings and the distribution of the cooling water under pressure. The complication here is only apparent, for the various devices are strong, easy of access and not exposed to high temperature. The slight increase in the cost of the plant is fairly compensated for by the advantages derived from the rotary movement. The metal becomes more homogeneous when given this motion.

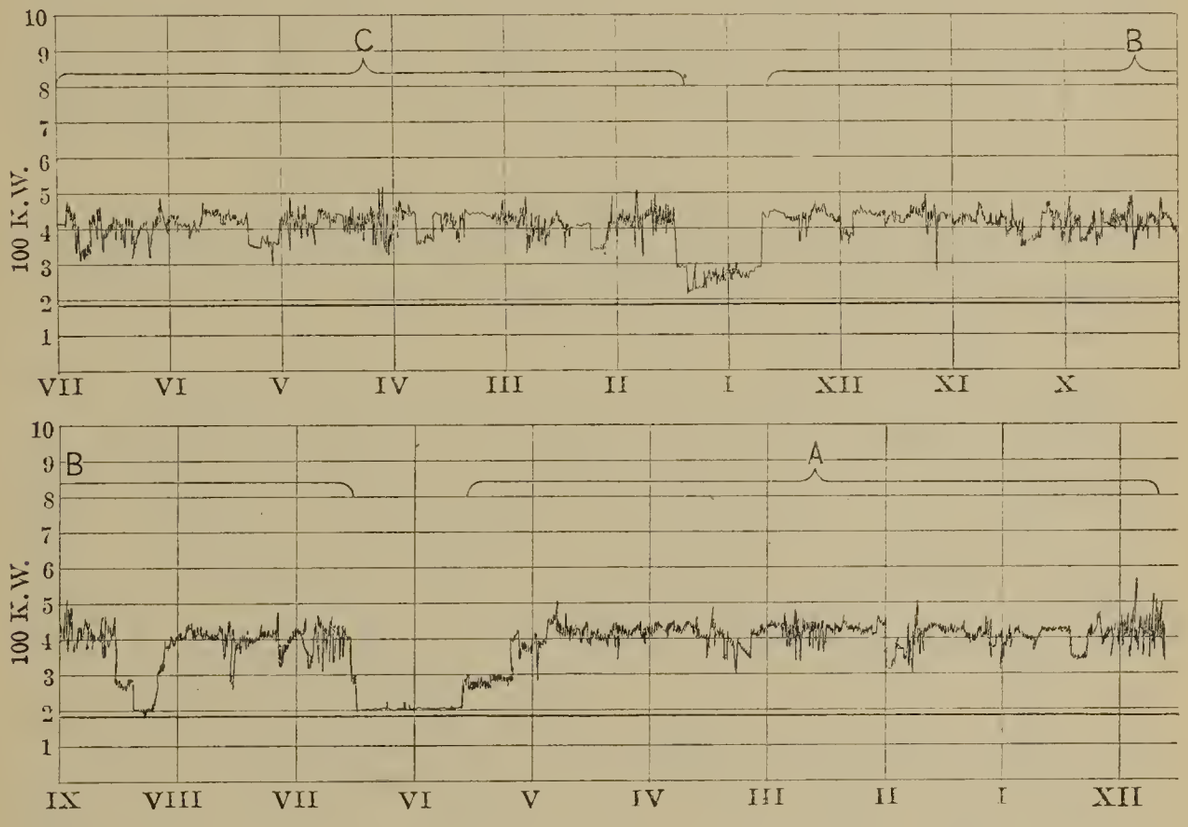
Still less is there reason for the two criticisms which seems to end in a contradiction. It is true that I demand more severe work from the lining in my furnaces than it has to stand in other arc furnaces. The bath exposed to the influence of one or more arcs is heated as much as in other arc furnaces, while the reflection of heat from the walls and roof outside of the bath does not in the least diminish their stability. In any case the bath in my furnaces is sufficiently hot.

As there is no current of air passing through my furnaces, the arc or arcs assume the quality of that obtained in a tightly closed vessel. The arcs are quiet and long and drive off the gases which escape over the whole surface of the bath at the highest temperature. Everyone who has seen my furnace working will note that the most elevated temperature may be reached without any trouble.

I have brought with me a diagram of the wattmeter registering one day's work at our Turin works. Two furnaces of 200 horse-power, and all the machine tools in the shop were running simultaneously, and yet the greatest regularity is shown. This regular consumption of energy permits me to use my furnaces in

any locality. It is evident that the largest production from the charge can be obtained. The consumption of electrodes is small, and this is because of the neutral atmosphere in which they are contained, both as regards the casings and the melting chambers where no current of air can penetrate, so that if there is a greater wear of the lining this is largely compensated for by the other advantages obtained.

Allow me to submit certain statements which at once will sustain my assertion and also show the real value of the complications attributed to my furnaces as compared with other systems.



To supply a furnace of my invention having a capacity of 600 kilowatts, a cable having a carrying capacity of 5,400 amperes is required. This conveys the energy of a single phase current of 150 volts and is divided up between four electrodes having a cross-section of only 135 square centimeters. In a similar furnace using a conducting bottom, the cable would need a carrying capacity of 16,000 amperes and one or more electrodes with a total cross-section of 4,000 square centimeters. A two-electrode furnace with a non-conducting bottom would require cables having a carrying capacity of 8,000 amperes, and the two electrodes would have a cross-section of 2,000 square centimeters each.

Having compared my furnaces with others and demonstrated that no serious criticism could be maintained against the former and that they at least stand on the same plane, I wish now to consider the difference of working in the case of the arcs and the induction furnaces.

It is well known that metals are refined by melting them in contact with a slag composed of ingredients which will absorb the impurities. These two qualities must be possessed by the slag; one to be refining and the other great fluidity. The latter quality requires the highest temperature which is easily obtained in an arc furnace, but not so in a furnace of the induction type. In the arc furnace the slag is submitted to the direct action of the arc and hence to the highest temperature while in the induction furnace the metal will be hotter than the slag, and consequently the latter is in an unsatisfactory condition.

At this point the question will be asked what advantages may be derived from the use of electric furnace in the metallurgy of iron and steel?

Apparently the most important of these advantages is that the electric furnace does not depend for its heat upon fuel, and consequently can be installed where fuel is lacking and where water powers can be obtained. Besides this, however, other qualities extend and generalize the field of application of the electric furnace, making it suitable as a useful auxiliary to metallurgy, even where the electric energy is generated by steam, etc.

The high temperature which can be obtained and, when properly constructed the possibility of working with exclusion of air, are advantages which are far from being found in fuel heated furnaces. Metallurgy has already made use of these qualities and the new system of heating is the exclusive property of none of the various systems of electric furnace, but is common to all. Consequently the only question is which of these apparatus utilize the heat to the best advantage? This is the capital point in the practical application of this new and powerful invention:

It is known, however:

(a) That all chemical reactions increase in activity with increase in temperature.

(b) That by increasing the temperature and consequently the fluidity of the metal that has to be refined, its dissociation from

impurities is much facilitated and their elimination is far more easy and rapid.

(c) Moreover it is evident that working with the exclusion of air, reagents may be employed to eliminate these impurities, the use of which otherwise would be quite impossible in the presence of atmospheric oxygen.

PART II.

(Translated by J. W. Richards.)

The simple statement of these facts themselves shows clearly why steel made in the electric furnace is of better quality than that made by ordinary processes, even starting with the same primary materials.

I might refer to another subject, but it is unnecessary to insist here on this argument. In examining the processes of refining iron and steel for which special processes exist we will examine the electric processes to see if they offer anything new.

In practice by the expression "refining of iron and steel" is understood the special operation by which, basing the process upon primary materials, cast iron or scrap, one removes the largest possible amount of dangerous elements, sulphur and phosphorus, and reduces to the required percentage the content of silicon, manganese and carbon, which, although not dangerous to the metal, change its properties.

From the beginning of the manufacture of steel on a large scale in a melted condition it has been recognized that one should:

(1) Oxidize the bath thoroughly in order to decarbonize as far as possible, and to remove, before the carbon, silicon and manganese in the presence of an excess of lime in order to eliminate as completely as possible phosphorus or sulphur; an oxidation produced directly by the oxygen by air existing in the furnace, or by additions of iron ore. (The ore process).

(2) Deoxidation of the metal by additions of silicon, manganese and carbon, after having removed the slag containing the impurities of the metal treated, replacing at the same time in the metal the desired quantity of silicon, manganese and carbon, and making it possible to eliminate with the appropriate slag the

sulphur still contained in the metal, in the state of sulphide of manganese or sulphide of calcium. Basing our process on that which has been just explained, and about which there is no shadow of doubt, we will examine in detail the various processes of refining iron and steel in the electric furnaces which have been proposed as new. We will see, however, that there is nothing new in that idea, because they utilize the reactions explained above, which were already known long before the first electric furnace was put in operation.

In consequence of what has already been said, and in reference to the special quality of the manner of heating these new furnaces, the greatest advantage may be taken from these reactions, to an extent characteristic of the manner of heating, and not of any particular electric furnace.

Great difficulties are met with in ordinary furnaces in obtaining a high degree of refining, along with great homogeneity or soundness of the metal, difficulties not depending on lack of knowledge of the refining reactions, but difficulties characteristic of the furnaces using combustibles as the source of heat.

In order to be able to eliminate the dangerous elements from the metal, and in particular phosphorus, it is necessary to decarbonize almost completely; during this operation the silicon and manganese oxidize and pass into the slag, and also some iron is oxidized.

The oxide of iron produced passes partly into the slag, and partly dissolves in the metal to which it gives injurious properties, making it unsuitable for industrial use. With the final additions of silicon, manganese and carbon, added in the form of ferro silicon and ferro manganese, a large part of this difficulty is overcome, but not entirely in ordinary furnaces. This is because it is difficult to produce a pure product in the open hearth process or the Bessemer process, and here is the reason:

Because of the great fineness of distribution of oxide of iron in the bath, a certain time is necessary to permit it to be reacted upon by the additions made, time is necessary also for the oxide of silicon and manganese formed by the destruction of the oxide of iron, and which are distributed like an emulsion in the mass of the bath, to separate and rise to the surface. But because of the oxidizing atmosphere existing in the furnace rendering it

impossible to keep the metal the necessary time for accomplishing these reactions, it is necessary to cast the metals.

It is just to obviate this inconvenience that for a long time the refining process has been done partly in the Bessemer, and partly in an open hearth furnace, because in the latter it is possible to work the metal under a slag, and to keep it longer submitted to the action of the final additions.

It has been attempted to reach also the same end by refining on a basic hearth of an open hearth furnace in order to remove phosphorus, and to complete the refining in an open hearth furnace having an acid hearth, after the elimination of sulphur. But working in an oxidizing atmosphere the results have not been brilliant; the oxide of manganese and silicon remained dissolved in the mass of metal, and the blow holes in the ingots prove the inferiority of steel obtained by the ordinary large scale processes compared with those obtained in the crucible.

It seems to me in place to add the results of two operations carried on at Turin in my works with an electric furnace operating 250 horse-power according to my system which confirms very well the above expressed views.

In the first of these operations it was proposed to obtain a semi-hard steel with about 85 kg. tensile strength per square millimeter, and at least 12 per cent. elongation. In the second it was proposed to obtain extra soft steel of 40 kg. tensile strength, and 30 per cent. elongation.

First Operation:

The current was put on the furnace at 1 P. M. working upon a charge of:

250 kg. of oxidized turnings;
450 kg. of scrap;
50 kg. of lime.

At 4 P. M. the charge was completely melted; the slag was removed after having taken a sample of the metal, and of the slag. The sample of metal was marked No. 1.

At 4.15 there was added:

50 kg. of cast iron;
1 kg. of ferro silicon, 50 per cent.;
6 kg. of ferro manganese, 80 per cent.;
15 kg. of calcium carbide in granular form.

At 4.40 P. M. the slag was removed a second time, and a sample marked No. 2 was taken from the slag.

After this there was further charged:

1 kg. of ferro silicon;

4.5 kg. of ferro manganese.

At 5 P. M. the metal was cast, and sample of the metal marked No. 2 was taken.

Resume.

Total weight of charge without additions	750 kg.
Weight of metal obtained	732 kg.
Weight of slag removed first time	120 kg.
Weight of slag removed second time	9 kg.
Loss during the operation	2.4 %
Consumption of electric energy during the fusion	555 kw. hrs.
Consumption of electric energy in refining	185 kw. hrs.
Total consumption per kg. of finished steel	1.01 kw. hrs.
Tensile strength of last sample per square millimeter	94 kg.
Tensile strength of last sample per square inch	134,000 lbs.
Elongation in 20 centimeters	14.5 %

(1) Analysis of Steel, Sample No. 1.

C	0.140
Si	traces.
S	0.076
P	0.018
Mn	0.120

(2) Analysis of Slag, Sample No. 1.

SiO_2	26.800
Fe_2O_3	3.420
FeO	15.430
MnO	4.252
Al_2O_3	9.22
P	0.890
S	0.360
CaO	32.720
MgO	6.150

(3) Analysis of Steel, Sample No. 2.

C	0.600
Si	0.300
S	0.015
P	0.020
Mn	0.990

(4) Analysis of Slag, Sample No. 2.

SiO_2	11.200
FeO	0.800
FeO	1.150
MnO	1.060
AlO	3.500
P	0.060
S	1.532
CaO	66.080
MgO	8.610

Second Operation:

At 12 noon the current was placed on the furnace, containing the following charge:

200 kg. of oxidized turnings;

750 kg. of scrap;

50 kg. of lime.

At 3.40 P. M. the charge was completely melted; the slag was

removed, and samples of metal and slag marked No. 1 were taken.

At 4 P. M. there was added:

100 kg. of cast iron;

15 kg. of calcium carbide.

At 4.40 P. M. the slag was again removed, and sample of slag, marked No. 2, taken.

At 4.50 P. M. there was charged:

50 kg. iron ore.

At 5 P. M. there was charged:

1.5 kg. ferro manganese, 80 per cent. Mn.

At 5.30 P. M. the metal was cast, and sample of metal, marked No. 2, taken.

Resumé.

Total weight of charge without additions	1,050 kg.
Weight of metal obtained	1,014 kg.
Weight of slag removed first time	105 kg.
Weight of slag removed second time	21 kg.
Loss during fusion	3.4 %
Electric energy used in fusion period	678 kw. hrs.
Electric energy consumed in refining	308 kw. hrs.
Total consumption of energy per kg. of finished steel	0.973 kw. hrs.
Tensile strength of final metal per square millimeter	72 kg.
Tensile strength of final metal per square inch	60,000 lbs.
Elongation in 20 centimeters	34.8 %

(1) Analysis of Steel, Sample No. 1.

C	0.070
Si	traces.
S	0.068
P	0.010
Mn	0.210

(2) Analysis of Slag, Sample No. 1.

SiO_2	18.90
Fe_2O_3	2.42
FeO	24.20
MnO	2.03
Al_2O_3	7.78
P	0.80
S	0.42
CaO	33.90
MgO	7.70

(3) Analysis of Steel, Sample No. 2.

C	0.080
Si	0.020
S	0.020
P	0.010
Mn	0.300

(4) Analysis of Slag, Sample No. 2.

SiO_2	12.09
Fe_2O_3	1.06
FeO	5.30
MnO	0.85
Al_2O_3	5.20
P	0.07
S	1.73
CaO	67.80
MgO	5.10

In these two operations the metal was quiet when cast, and the ingots were free from blow holes with the exception of the

inevitable pipe due to contraction. From the above tests and results it can be deduced:

(1) That the refining took place according to well known reactions.

(2) That the periods of deoxidation and desulphurization may be prolonged in the electric furnace the necessary time for the completion of the reactions.

(3) Since the atmosphere of the electric furnace is neutral, the calcium carbide may be used as a deoxidizing and a desulphurizing agent, utilizing reactions already well known, but impossible of being produced in the ordinary furnaces because of lack of this neutral atmosphere.

Having analyzed the technical advantages of the electric furnace, I will take up the financial questions connected therewith, for if only the electric treatment of iron and steel can be done economically with advantage, the problem of thermo electric iron metallurgy may be considered as definitely solved in a practical way. In my previous publications I have already taken up this question, and not repeating what I have before said I will present my conclusions drawn from my experience. According to these, even with furnaces of small capacity, the refining of cast iron and scrap using cold metal can be accomplished with a consumption of 1,000 kw. hours per ton. Naturally this consumption of energy is reduced in furnaces of larger capacity; thus with an apparatus of 1,000 to 2,000 horse-power one can reach an energy requirement of 800 to 700 kw. hours per ton. To this expenditure of energy must be added the expense for electrodes, which in my furnaces have amounted to 8 or 12 kg. per ton, including the useless stub ends.

The cost of labor including management, depreciation, etc., are about equal to that in an ordinary steel works; on the contrary the maintenance of the furnace—refractory material—is higher because the temperature is higher at which the reactions in the funace proceed, but if one considers the small loss of metal during fusion, and the efficient utilization of the deoxidizing agents resulting from the neutral atmosphere in the furnace, it is seen that this extra expense is compensated for by other considerations.

In consequence, one can say without fear of being in error

that the difference between the cost of manufacture of steel in the electric furnace, and in the ordinary furnace rests solely in the difference between the cost of the electric energy and electrodes for the electric furnace, and of the fuel for ordinary furnaces, and this without taking into consideration the superiority of electric furnace steel.

It is easy therefore to see that even under these conditions the advantage would be in favor of the electric furnace steel, even if its price was slightly higher, because of its superior quality.

If one takes as a basis the price of 30 centimes to 40 centimes per kg. (3 to 4 cents per pound) of electrode, 1 centime to 2 centimes (0.2 to 0.4 cent) per kw. hour of electric energy obtained in hydro electric plant, it can be seen that the price of production of a ton of steel, starting with cold charges will be between 14 and 24 francs ($2.80 and $4.80) per ton for small plants, and from 11 to 18 francs ($2.20 to $3.60) per ton for larger plants.

If one considers that for a daily production of four to five tons it is necessary ordinarily to use the costly crucible plant, burning nearly two tons of coal per ton of steel produced, and that for the Siemens-Martin furnace 300 kg. of coal is required, in large furnaces for the same amount of steel, it may be concluded:

(1) That with electric energy costing from one to two centimes (0.2 to 0.4 cents) per kw. hour the electric furnace, starting with scrap and pig iron will be always profitable in small installations, while for larger, and quite large plants, it would be profitable only under particular circumstances where fuel is scarce, and ore is very dear.

(2) That for replacing the crucible the electric furnace will be always the more advantageous even if one is obliged to produce the electric energy either by gas or steam engines.

(3) These various applications will be quite sufficient to assure the success of the electric furnace, but there are two other applications which will enlarge still further this field of application, and which I should not pass over in silence.

(4) In the preceding part of my paper where I have referred to the various methods of refining iron and steel I have mentioned that the faults of the ordinary furnaces are specially in evidence during periods of deoxidation, and of refining, and I

added that to obviate these inconveniences recourse was had to commencing the refining in one furnace, and finishing it in another. If then, in place of transferring the steel of one ordinary furnace into another, it is made in an electric furnace which, as I have already said, lends itself admirably to deoxidizing, refining and finishing the metal, a degree of perfection can be obtained which in spite of all efforts has so far not been attained.

(5) It is not without intention that in the example given above I have divided the consumption of electric energy into two parts, that is, (1) that necessary for melting the metal and decarborizing it, and (2) that necessary for its refining and finishing; this latter being in small furnaces from 200 to 250 horsepower not above 200 kw. per ton of metal obtained. In these conditions it is seen that the expense of electric energy itself even if produced by gas motors or steam engines may be largely compensated for by the advantages of the improved product which in the near future opens a door to a large use of the electric furnace for completing the refining of steel.

(6) The second application I would speak of is in the direct manufacture of steel from iron ores. This demands, in order to be economically produced, motive force very cheap and working upon a large scale. According to various tests which I have made in this direction it is certain that with a consumption of 3 kw. hours per kg. per product obtained, and of 15 to 20 kg. of electrodes per ton of metal, one can obtain steel from the ores directly, of very good quality, and at a cost price not higher than that of steel obtained in the Bessemer converter using required cast iron direct from the furnace.

(7) There remain yet several things to be said about the electric furnace, but to remain within the limits of a general paper such as this I conclude by recapitulating as follows:

(1) None of the electric furnaces to-day in operation are constructed on new principles, and no one of them is particularly superior to any of the others, at least in their characteristic details.

(2) That none of the methods employed of the metallurgy of iron and steel in the electric furnace as operated to-day may be called novel.

(3) That from tests already made we can say that the electric

furnace is no longer in its infancy, but on the point of industrial application.

(4) In consequence of these facts, if the practical men will drop their usual mistrust of new things, and will become persuaded by the advantages to be obtained by the electric furnace, and will try to find amongst the different types the one most applicable to their special case; and if further, the inventors of these different types of furnaces will become convinced that none of them have special rights to the whole field, and that their apparatus differ amongst each other in special details of construction; and if further, in place of criticising each other they will properly recognize the importance of this new field opened to this industry, then we will see in a short time the electric furnace highly developed, bringing to the iron and steel industry, and to the inventors themselves, numerous and almost inestimable advantages.

DISCUSSION.

Prof. J. W. Richards: I know from conversation with the Major that it is his opinion that economy of heat is obtained by having the source of heat at as high a temperature as possible.

In speaking with the Major, at his works in Turin, about the criticism that his furnace was complicated, he said: "Yes, the furnace looks complicated, it has a great many parts; but so has a locomotive. Yet a locomotive works very well."

I have seen the furnace in operation, and I was surprised to notice the very small amount of heat radiated from the furnace. The walls are about 18 inches thick, the outside of the furnace was cool enough to place the hand on without burning, and the heat on the inside was quite all that was necessary for the dead smelting of soft steel. In fact, I saw the steel tapped from the furnace into a ladle, and the last drop of the steel poured out of the large ladle into a small ladle.

In the Major's foundry he has at least 100 men working, and is casting metal made in these furnaces into commercial steel castings, which he is selling in competition with other steel castings made by the Bessemer and the open hearth process—ordi-

nary steel castings. He has impressed on me the fact that he has not taken the time to make special steels, or high grade steels, but he is making ordinary casting steel and turning it into castings which are being moulded and sold in competition with ordinary steel castings.

Prof. S. A. Tucker: I would like to ask Major Stassano how the refractory lining of his furnace above the slag line is kept from melting; as the radiant heat is sufficiently intense to keep the basic slag molten, it would seem as if the lining would be melted.

Maj. E. Stassano (*Communicated*): In response to the question as to the life of the refractory lining of my furnace, I beg to say the lining is made of magnesia brick. Its life when working continuously is from three weeks to one month, after which it must be entirely replaced. But during this interval of three to four weeks, *no repairs whatever* are made to the furnace. The reason the lining does not melt, while the basic slag does, is because the lining is more refractory than the slag.

A paper read in abstract by Mr. P. McN. Bennie, at the Fifteenth General Meeting of the American Electrochemical Society, at Niagara Falls, Canada, May 6, 1909; President E. G. Acheson in the Chair.

A CONTRIBUTION TO THE STUDY OF ELECTRIC FURNACES AS APPLIED TO THE MANUFACTURE OF IRON AND STEEL.

By Charles Albert Keller.
Managing Director of the Société des Etablissements Keller Leleux, Livet Works, Isère, France.

(Translated by P. McN. Bennie.)

Part I.

Development of Industrial Electric Steel Furnaces.

Although but an innovation of yesterday, the electric furnace manufacture of steels has already grown into a most captivating subject, by reason of the new industrial results produced, and and those which are as yet but half disclosed. To treat of the subject in its entirety would require entering into very extended considerations, which I do not wish to do in this memoir.

In response to the kind invitation which the American Electrochemical Society has done me the honor to extend, I propose to present to this assemblage an account of certain personal researches and work upon the manufacture of electric furnace steels; my purpose is to add another stone to the edifice, convinced, as Harmet has so well said, that "stone upon stone, the structure rears."

The application of electric furnaces of the "electrode" type to the fabrication of metals which must be won, melted, or transformed out of contact with carbon, and more particularly the solution of the problem of making steel, created the necessity of so making the conducting hearths or bottoms of such furnaces as not to carburize the liquid metal contained therein.

The conducting bottoms of electric furnaces currently used for

electrometallurgical manufactures (calcium carbide, ferro-silicon, ordinary ferro chromium, etc.) have from the very first been made either of a rammed mixture of carbon and a binder, or built up with pieces of electrodes, the carbon lining thus formed being connected in various fashions with one of the poles of a source of energy, the other pole being connected to one or more electrodes placed vertically in the furnace.

Although it is only within recent years that the types of furnaces using conducting hearths or bottoms have been worked on the industrial scale with materials other than carbon, it should, however, be borne in mind that the making of a conducting bottom without carbon had been done long before and used at various periods. If no industrial electric furnaces followed this realization, it was principally because the construction of a practical metallic conducting hearth, or of a hearth containing a metallic pole, presented greater difficulties than the simple carbon hearth. Also because the need for a non-carburizing hearth had not then made itself felt in the electrometallurgical art, save for some unimportant lines of manufacture, where the methods used were made a matter of great secrecy, and not divulged by those using them.

When the problem of the electric furnace manufacture of *steel* became a live one, it created the necessity for the non-carburizing conducting hearth.

On the other hand, it has been known since the practical use of the electric furnace first began, when dealing with products giving rise to a slag (treatment of chrome ores, for example) that regulation of the arc voltage requires the compulsory maintenance of the end of the electrode in this slag, or above it, since contact with the metal would at once cause a practically complete short circuit.

It becomes evident then that given a non-carburizing hearth already in use, the electric furnaces in the existing electrometallurgical works were, in principle, all ready for the manufacture of steel, since the upper electrode by its obligatory position electrically when working, cannot of itself effect carburization of the bath in the furnace. Then to better fit such furnaces for metallurgical operations, it should only be necessary to supply

them with details already known and applied to certain electric steel furnaces (charging doors, rockers or rollers for tilting movements, air-tight covers, etc.), which would not introduce any difficulties or hinder the rational study of an electric furnace based upon the use of a conducting hearth to carry the current.

At the present time, non-carburizing conducting hearths may be divided as follows:

(I) *Simple Conducting Hearths:*

(a) Having the entire furnace bottom of metallic material.

(b) Having one or more metallic poles embedded in a non-conducting masonry.

(c) Having the entire bottom of a conducting rammed material.

(II) *Compound Conducting Hearths:*

I shall here more especially describe a system worked out by myself, consisting of a type of mixed or compound conducting hearth.

Nevertheless, to precisely define why this system is thus classified, and what differentiates it from the other types, I shall briefly describe the first category and its various sub-divisions mentioned.

(I) Furnaces With Simple Conducting Hearth:

(*a*) *Entirely Metallic Hearths:*

Several types of furnaces have been conceived where the hearth is made of soft steel, cooled by water circulation, but these have not had important commercial application; they are simply mentioned as a type. The high temperature of the liquid metal does not permit maintaining a metallic bottom, even when cooled, except with an excessive loss of heat, and constant danger.

(*b*) *Simple Conducting Hearth, consisting of one or more metallic poles embedded in non-conducting masonry:*

In such furnaces one or more metallic poles are embedded in the masonry of the hearth, the current passing through the metal pieces; these conductors are connected at their outer extremities with one pole of the source of energy. This type of furnace is

distinguished by the fact that the current is confined almost entirely to the metallic pole, or poles if it is divided into several parts, by a refractory non-conducting masonry, the masonry surrounding them closely as protection against infiltration by the liquid metal.

Siemens' Furnace:

The first furnace displaying this type was installed by Siemens[1], who contrived a furnace composed of a movable vertical

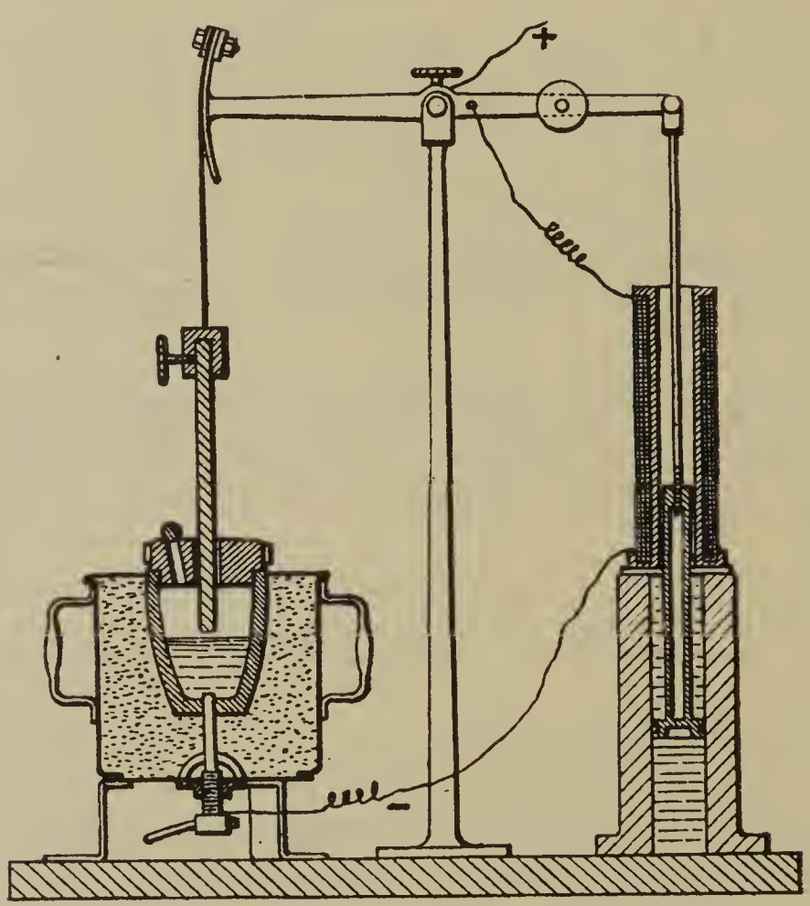


Fig. 1.—Siemens' Furnace.

electrode (Fig. 1) connected to one pole of the source of energy, the other pole being connected to an iron bar passed through an opening in the bottom of the furnace chamber. This chamber was surrounded by a heat insulator, and later Siemens adopted a method of water cooling the metallic pole to prevent its destruction. Regulation of voltage was effected by an automatic solenoid regulator.

[1] Elektrotechnische Zeitschrift 1880, Communication of Siemens.

Borchers' Furnace:

A very distinct type of furnace was invented by Borchers[2] (Fig. 2).

An iron casing having a bottom of refractory brick is lined with a suitable material. In the bottom lining is placed a block of steel, into which screws a copper tube, used for circulation of the cooling water for the metallic steel poles. The steel block

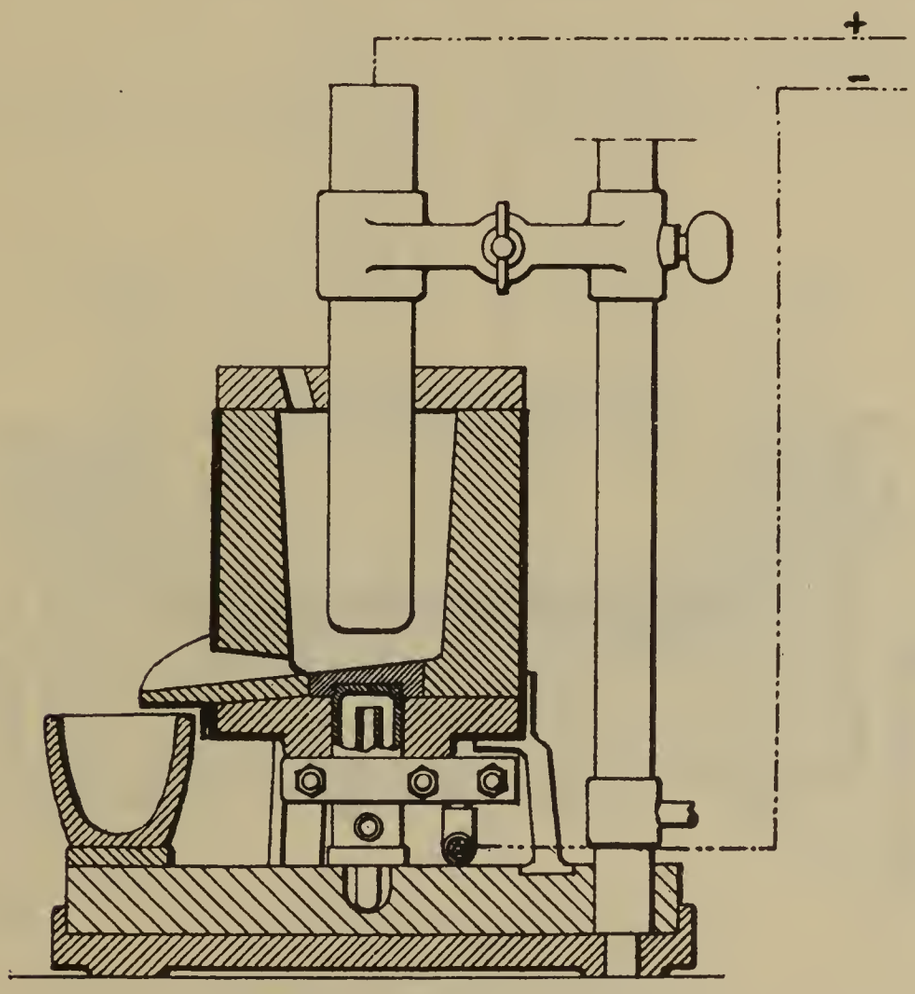


FIG. 2.—Borchers' Furnace.

thus cooled is connected at its lower extremity, to one of the poles of the source of energy, the other pole being connected to a vertical electrode, movable for the purposes of voltage regulation. During the working of the furnace the metal which collects at the bottom is tapped from time to time, while the gases escape through openings in the cover.

In spite of the surpassing electrometallurgical feats of Siemens, who, at the Electrical Congress at London, in 1880, publicly

[2] Traite electro-metallurgique de Borchers, 2 *eme* Edition, 1896.

showed, with his metallic pole furnace, a cast of about 45 pounds of steel, this type of furnace did not have an immediate industrial future.

The electric furnace manufacture of steel, for which such a furnace could have been used, had not yet become a live question, so it remained neglected until it should become so, roughly speaking in 1905, when we find the furnace with metallic poles revived by Girod, who installed several of them.

Girod's Furnaces:

Girod took a patent in 1905[3] for a type of furnace having

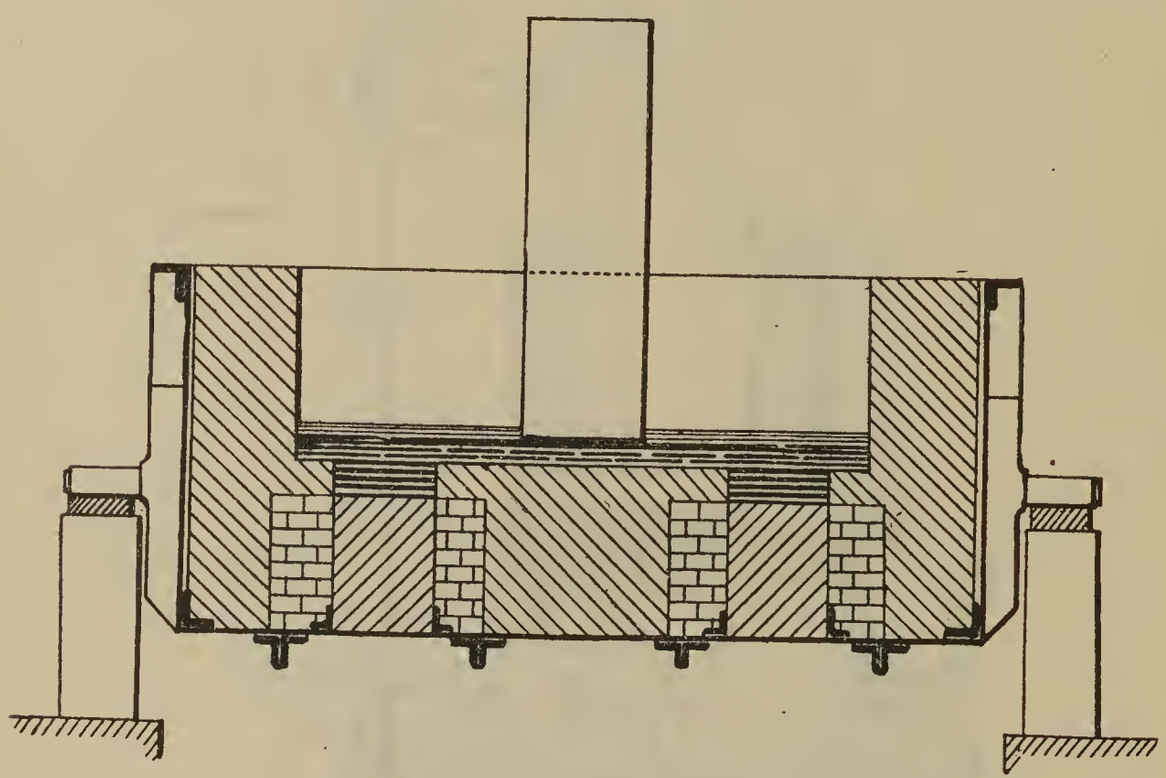


FIG. 3.—Girod Furnace.

metallic poles embedded in the hearth, which he indicated could be constructed in three different ways.

The poles might be either of graphite or metallic. If of graphite (Fig. 3) before being put into service they are covered with a metallic coating to preserve the metal under treatment in the furnace from carburizing by contact with the graphite. The poles in the hearth are, therefore, in this case of graphite surmounted by a metallic head similar to the metal to be obtained in the furnace.

[3] French Patent No. 350,524, January 4, 1905.

The second arrangement (Fig. 4) admits of the use of one or more poles, entirely metallic, cooled at their lower ends, and terminating at their upper ends in canals placed in the masonry of the hearth; these canals or channels are previously filled with metal of the same character as it is desired to obtain in the furnace. This metallic covering after solidification protects the metallic poles proper, because the heat of the furnace would not

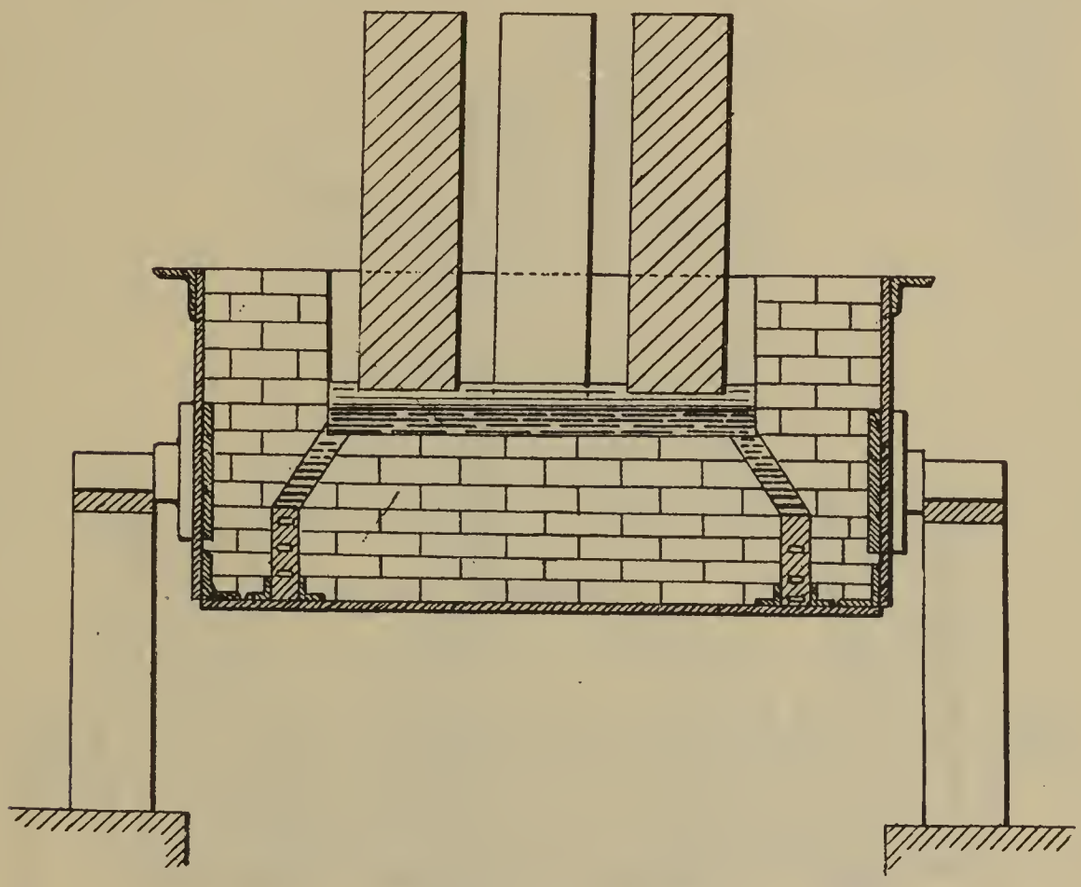


Fig. 4.—Girod Furnace.

melt them out entirely, in view of the artificial cooling of the lower ends of the metallic pole pieces.

When a number of such pole pieces are introduced into the hearth they are, of course, connected in parallel outside of the furnace. In any case the poles are separated from each other by the refractory material of the hearth, and furthermore are surrounded by a masonry of refractory brick, selected of such nature as not to become conducting when heated.

Having thus arranged the hearth of his furnace Girod provided the working chamber of the furnace according to the practice already employed for construction of existing electric steel

furnaces, fitting them with charging openings, proper roofs, etc.; finally he made the whole furnace tilting, either by means of trunnions or rollers, according to known means.

The use as indicated of one or more metallic poles bedded in masonry (the latter not carrying current) implies a distribution of energy through divided lines of flow from the superposed electrode, the current thus being forced to traverse the layer of metal under treatment in the furnace, according to Fig. 5.

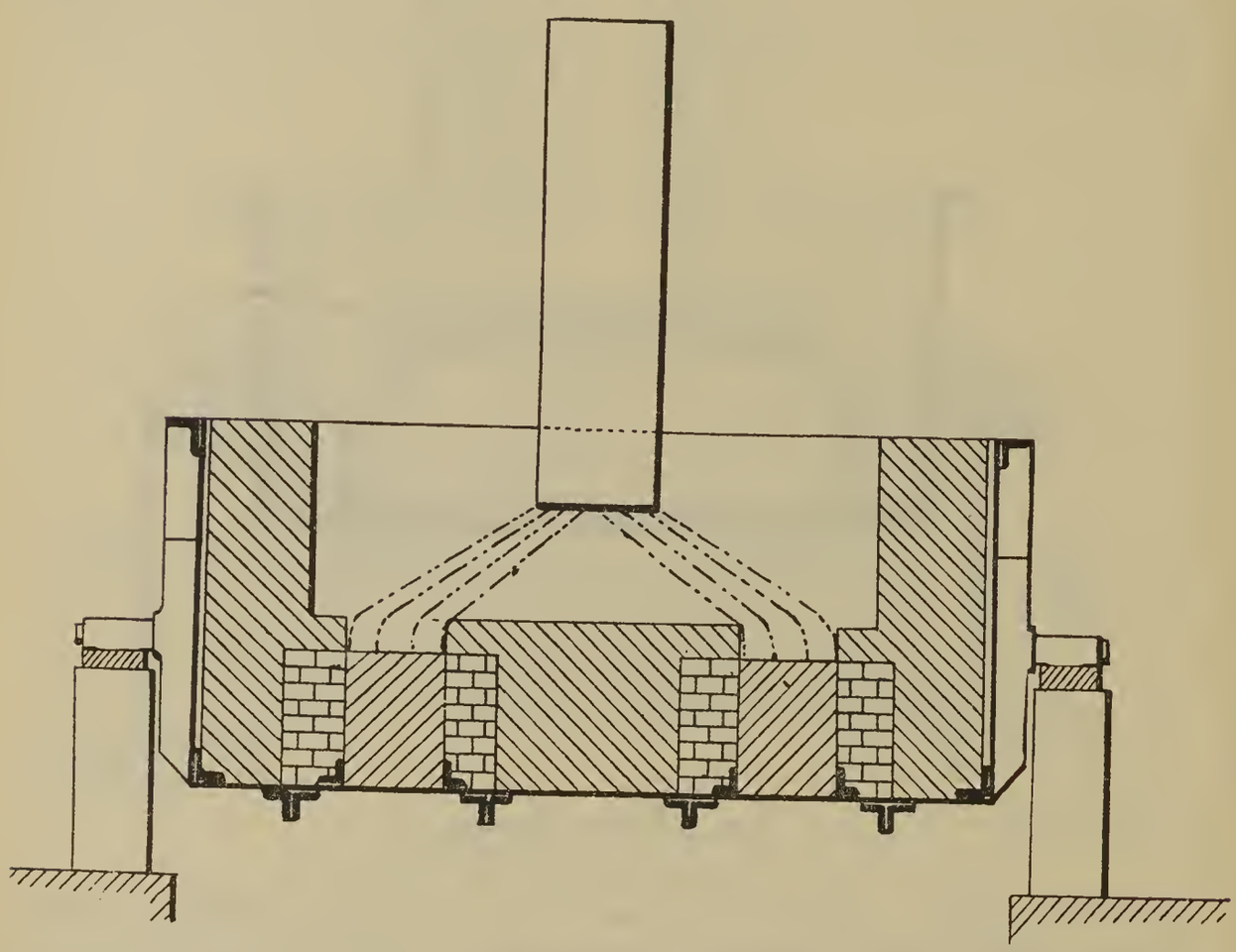


Fig. 5.—Lines of Current Flow in Girod Furnace.

The third arrangement indicated by Girod consists in placing the metallic pole in the masonry of the lateral wall at the point of contact between the side and bottom of the furnace. In this case the hearth proper does not carry any conductor (Fig. 6).

Following this line of ideas several types of furnaces have been created. I shall refer to this later, apropos of furnaces with vertical electrodes for both poles of the circuit.

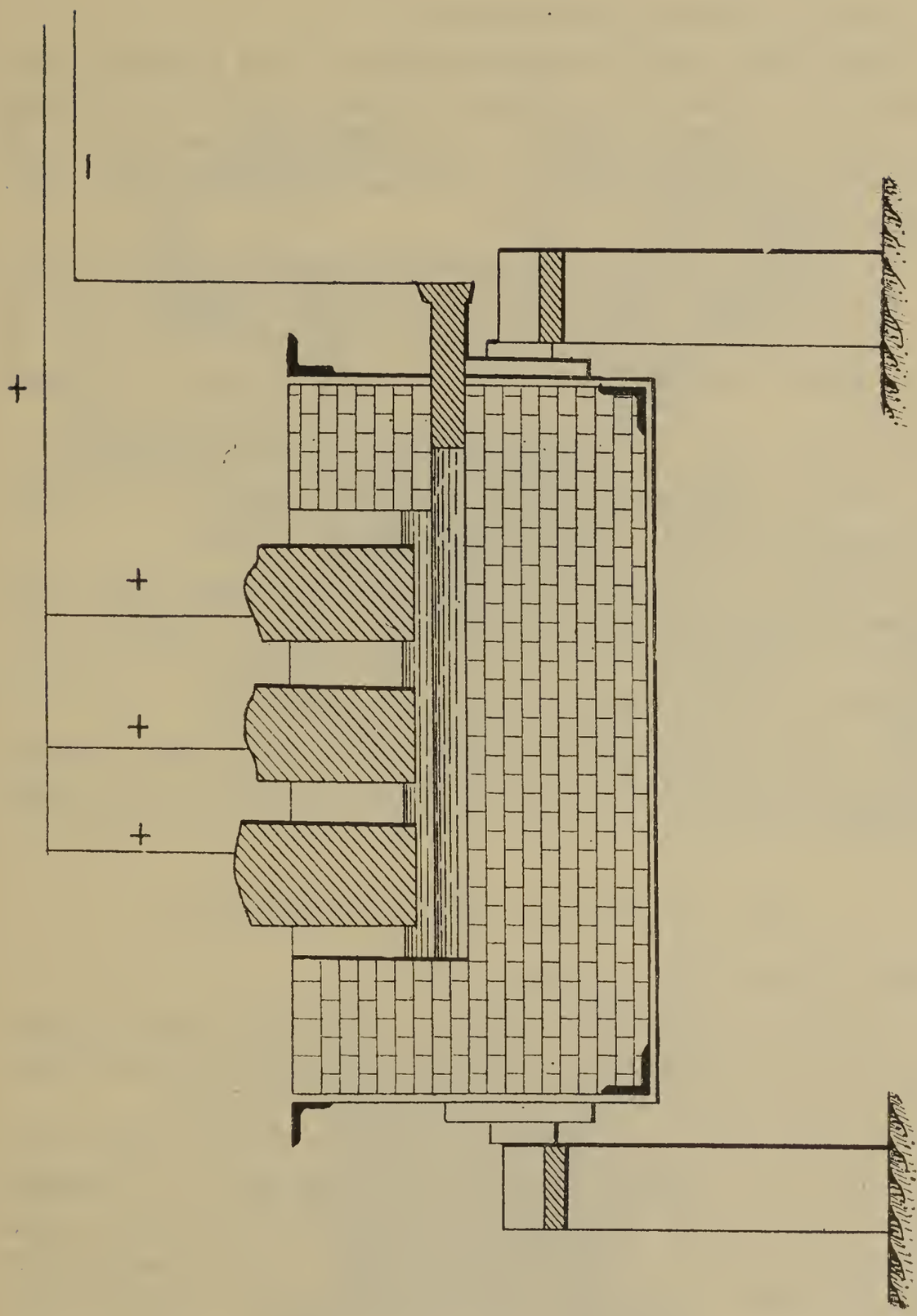


FIG. 6.—Girod Furnace with Lateral Pole in Heart.

(c) Conducting Hearth Obtained by Use of a Rammed Conducting Lining:

Furnace of Firminy Steel Works[4]*:*

Under this system the hearth does not have a metallic conductor; it is formed of a refractory mixture rendered conducting by the introduction of carbon, or carboniferous material (coal tar pitch) into the refractory material (magnesia, silica, etc.) chosen for the mixture, or pisé.

The carbon content of the material is progressively increased at different levels in the depth of the hearth, so as to utilize at the beginning of a run the variations in electrical conductivity of the rammed mixture, according to their content of carbon material.

The upper layer of the lining mixture which comes into contact with the steel is formed of a mixture quite low in carbon, so as not to influence the carbon content of the steel.

According to the inventors the crucible having once been heated becomes permanently conducting no matter what the variations of temperature of the furnace; consequently re-starting from the cold state becomes practically possible.

The Firminy Steel Works, where this furnace was invented, have constructed up to the present time only one furnace of small capacity.

(II) Compound Conducting Hearths:

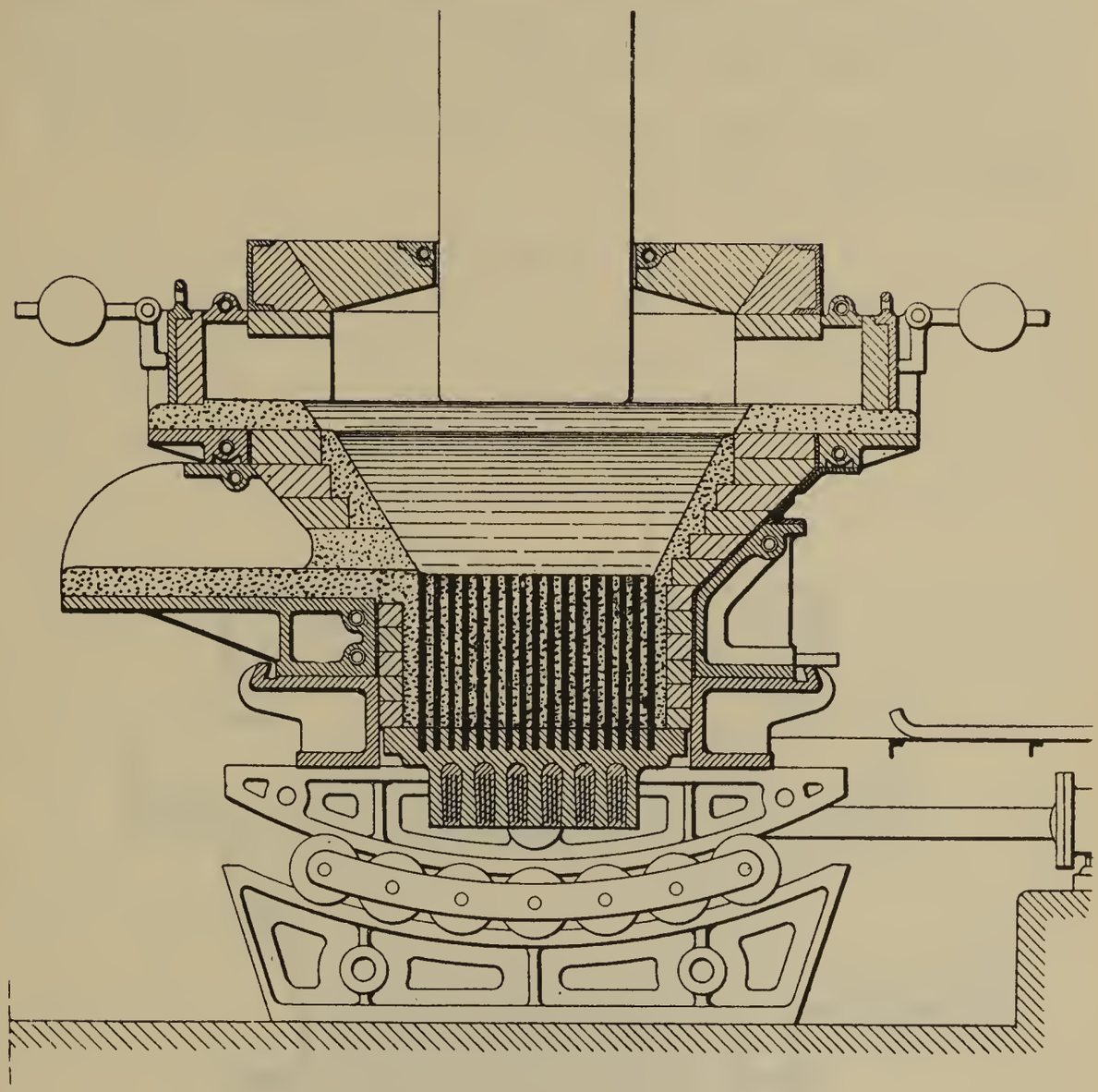
Charles Albert Keller Furnace:

I worked out and put to industrial use two years ago, an electric furnace of which the conducting hearth is composed of electrically reinforced pisé (pisé armé) made as follows:[5]

Iron bars 1″ to 1¼″ diameter, regularly spaced about 1″ to 1¼″ apart, are placed vertically and made firm to a metallic plate at the bottom, the group of bars thus covering the entire area upon which the liquid bath will rest. A pisé consisting of a basic material conductor of the second class (magnesia preferred) agglomerated in the ordinary manner, is strongly rammed

[4] French Patent No. 387,747, March 4, 1908, and Certificate of Addition No. 9,272, May 1, 1908.

[5] French Patent, Ch. A. Keller, No. 393,740, November 4, 1907.



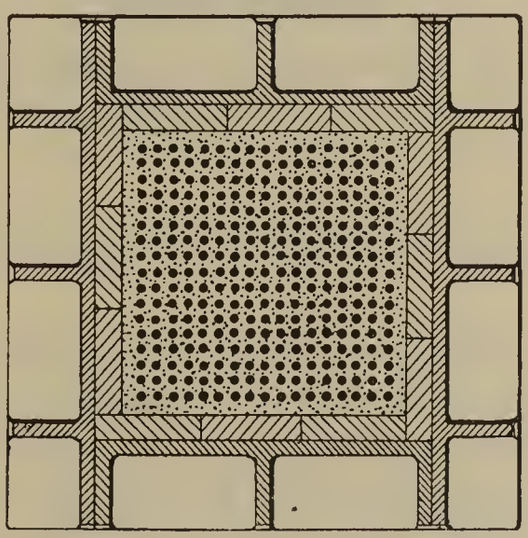


FIG. 7.—C. A. Keller Conducting Hearth Furnace.

while hot between each group of four adjacent bars, which thus form by reason of their mechanical strength, a sort of mold, permitting considerable compression of the mixture introduced. The pisé thus formed must be driven home by means of a suitable rammer. (Fig. 7.)

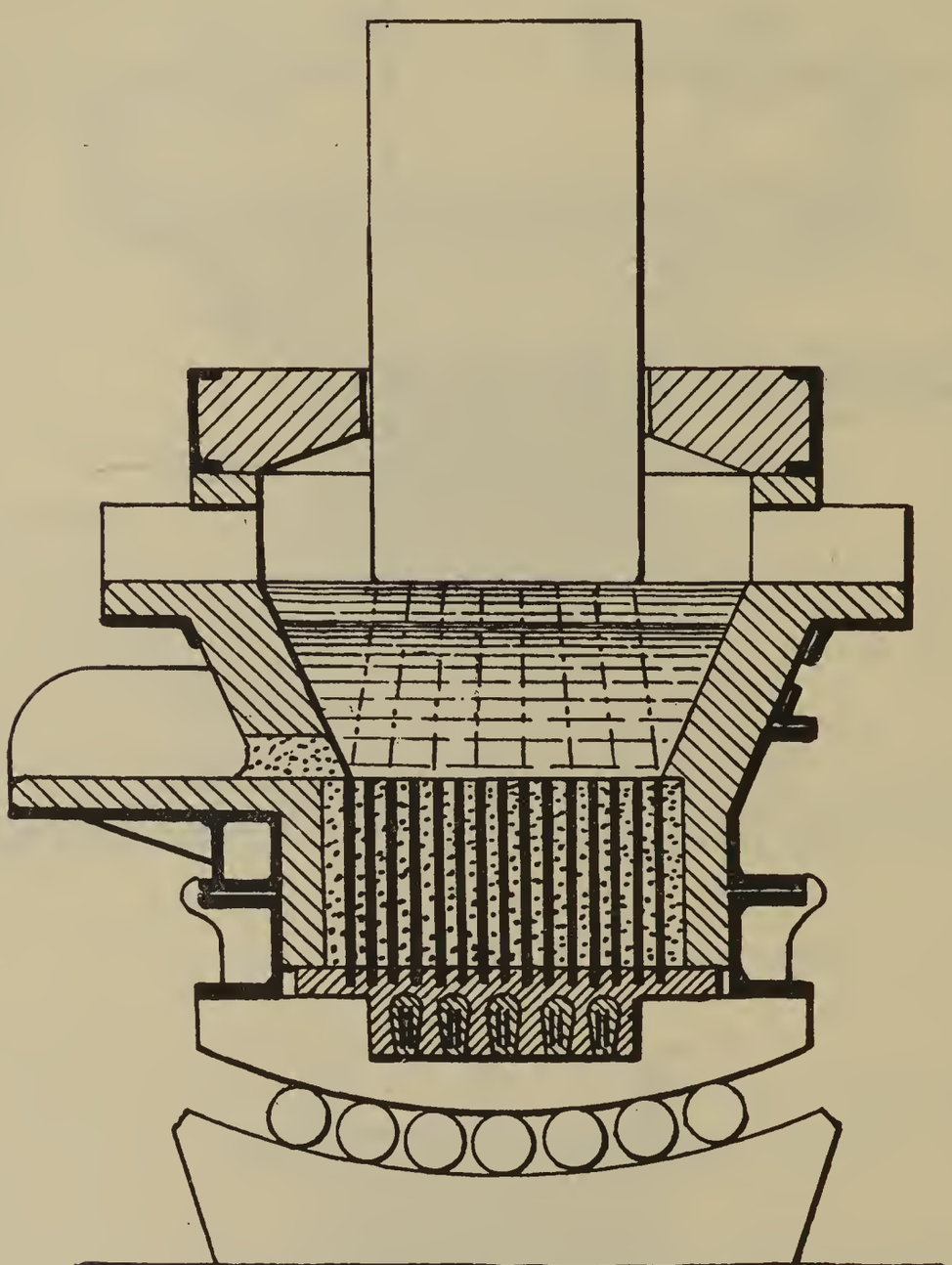


Fig. 8.—Lines of Current Flow in Keller Furnace.

There is thus obtained an extremely compact mass or block of compound nature consisting of iron and refractory material, of which the metallic sections are good conductors when cold; when heated the pisé also rapidly becomes a conductor with the high temperature. The whole is surrounded by a metallic casing

serving as an envelope which may be cooled by a current of water. The lower plate fastened to these iron bars is connected to one of the poles of the source of energy.

The conducting hearth thus realized makes the starting up of the furnace very easy, because it is uniformly conductive throughout its entire transverse section, by reason of the iron bars near together, and terminating at the surface of the hearth. The small distance between the bars and the conductivity of the pisé practically places them electrically in parallel for their whole length when the furnace is in full operation. The distribution of the electric current is thus practically equalized throughout the whole section of the hearth.

The lines of flow of current which are produced in furnaces having isolated metallic poles are absolutely removed by the above arrangement (See Fig. 8) because the electric current from the upper electrode passes through the metal uniformly, and also in the same manner throughout the section of the hearth.

The electrical resistance of a conducting hearth constructed as described is almost negligible, because the area of the furnace bottom allows of the use of a large number of bars, representing a total conductivity so high that without considering the conductivity of the pisé the loss is negligible. Furthermore, the use of metallic conductors of small section produces a more rational flow of alternating electric current than the use of large sections.

It should be noted that this sort of hearth does not require any masonry whatever; the entire bottom of the furnace is filled by the transverse sections of the block, which is semi-refractory, homogeneously semi-metallic, a good conductor, and practically infusible at the working temperature of the furnace. The metal does not, therefore, rest upon a masonry bottom, but upon a compound body which is to the masonry of a hearth with embedded metal poles, what reinforced concrete is to ordinary masonry.

The mechanical resistance of the hearth to penetration by the bath is thus very considerable, and no deterioration by lifting of the bottom, splits or fissures, is to be feared. Finally the mechanical joining of the bars at their lower ends, and their intimate union by the pisé make the bottom block of the furnace abso-

lutely undeformable, a condition which cannot exist with free metallic blocks laid in masonry.

The entire bottom carrying current, starting up with an empty furnace can be accomplished with certainty and without loss of time.

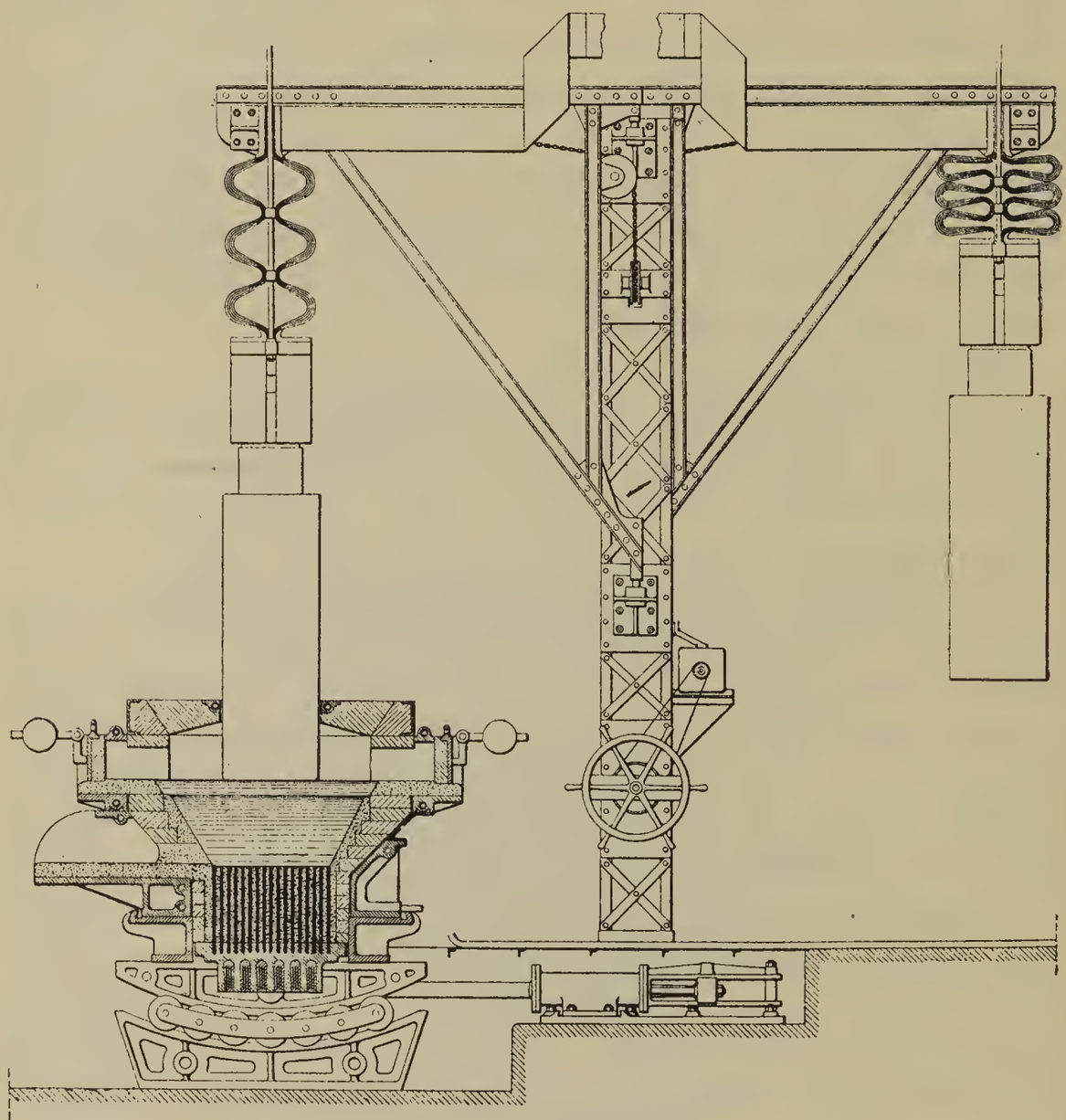


FIG. 8(*a*).—Keller Furnace. General Arrangement.

This conducting hearth block constitutes the original portion of the furnace, of which the working chamber is formed as ordinarily by a metallic structure lined with basic refractories strongly fastened and braced. The chamber is enlarged above the hearth for better support of the hearth block. The pisé is easily repaired through the charging doors, after tapping, when necessary.

The body of the furnace is cooled on its entire periphery at the upper level of the hearth, to insure protection at the junction of the lining of the working chamber with the hearth.

The furnace is closed by a cover, through which the electrode passes. The regulation of the electrode is accomplished either by hand or automatically; the latter is more simple and preferable.

To avoid shut downs, when replacing an electrode, the latter is placed at the end of a swinging arm, so that it may be removed out of the way and replaced by another electrode all ready at the end of a similar swinging arm (Fig. 8a); the changing of an electrode is thus accomplished in 2 to 3 minutes.

The electric furnace, as I have thus described it, allows of the use of one or more vertical electrodes which are arranged either of the same polarity and in parallel or upon each phase of a polyphase circuit. A three-phase furnace will require, it is understood, three electrodes, and if the star connection is used, the neutral point would be connected to the conducting hearth.

I have found that the hearth of a furnace of 3,300 pounds capacity, especially dismantled for inspection and study, after several months' service, was in absolutely as good condition as on the first day; the pisé having acquired an extraordinary hardness, comparable to rock, so that a chisel was blunted.

I am satisfied that such a construction supplies as simply and surely as possible a non-carburizing conducting hearth, permitting in an exceedingly simple and certain manner, metallurgical operations, eradicating all the ordinary annoyances of hearths, their repair and reconstruction; while at the same time providing an electrical conducting hearth free from appreciable industrial losses.

The manufacture of steel may be carried out to considerable advantage on a non-carburizing conducting hearth, of course on the condition that the design of hearth adopted is not a source of annoyance on account of frequent repairs.

Here a question arises as to the advantage which may be obtained with a furnace having a conducting hearth compared with a furnace having vertical electrodes in series, these serving for entrance and exit of the current, a type of furnace which

already has an important place in the history of the electrical manufacture of steel. After having made much use of electric furnaces with electrodes in series, of which I shall speak further on, I am convinced that the question which I propose above, and which I have heard proposed several times, is not without interest, and it was this which led me to carry out a parallel study of the two types of electric steel furnace. I undertook to investigate whether the passage of the current through the entire mass of molten steel, or its "complete electrification," possessed any real advantage as compared with the process of electric heating by superficial passage of the current characterizing the furnace with electrodes in series.

I believe that an electric furnace with a conducting hearth presents metallurgical advantages over the furnace with electrodes in series so far as concerns a furnace of low or medium capacity. In fact the method of heating which characterizes the furnace with a conducting hearth, on account of the current being forced to pass through the whole mass, is advantageous as regards the production of a metal having a thoroughly homogeneous quality. Moreover the furnace with a conducting hearth is of very simple mechanical construction; its starting and operation are more simple when it is used for the treatment of a cold charge; and again it must be noted that the preservation of the roof is easier with a furnace having a conducting hearth.

Yet a formal conclusion is a delicate matter, and I understand the hesitation of the metallurgist who has to compare the two types of furnaces when he desires to produce steels of very highest grade, because on *a priori* grounds and with considerable reason he would consider that the "electrification of the steel" may be advantageous as regards its homogeneity, and thus give the preference to the furnace with the conducting hearth, while at the same time he may be tempted by the greater ease of construction which characterizes a furnace having electrodes in series. It is a fact that the latter furnace does away with all electrical fittings in its lower part, since the entrance and exit of the current are confined to the upper part, and this is an important simplification. Moreover it should be remarked that in the latter type of two-arc furnace, with an equal rate of gen-

eration of energy, the current necessary is only one-half that in the furnace with the conducting hearth, which effects economy in the matter of electric conductors. The furnace with the conducting hearth necessitates a pretty large inductive loop, in which we have the body of the furnace itself, while this is outside the magnetic field in the case of furnaces having electrodes in series. The power factor may be lowered considerably in the first type of furnace if special precautions are not taken. It is necessary to resort to the construction of non-magnetic gaps in the furnace body, and its fittings; and in addition great care must be taken to avoid the use of fittings made of a metal of high magnetic permeability, such as wrought iron, cast iron or steel, inside the inductive loop. Although effective precautions are possible, they nevertheless present an appreciable difficulty in construction which is far from being so marked in the case of the furnace having electrodes in series, where the in-going and out-going path of the current is altogether outside the furnace body and its fittings.

Recapitulating, the electric furnace with a conducting hearth necessitates greater precautions in its practical design and construction than the furnace with electrodes in series; but it must be said that the engineer who is thoroughly familiar with alternating currents will know how to get around and avoid the difficulties which the problem presents, and even in a furnace of very large capacity may obtain a reasonable power factor. This is more particularly true if the engineer is allowed to design the whole electrometallurgical installation, for under such circumstances he will not fail to adopt a low frequency (20 periods for example) which will greatly simplify the design on account of the great reduction in the inductance of the circuit.

For example, I may say that according to my opinion, with a frequency of 20 periods a 1,000-kilowatt furnace may have a power factor of 0.9. Such a furnace used in the refining and finishing of molten steel will have a capacity of 10 to 12 tons. A furnace of greater capacity could be obtained with the combination of several similar elements, that is by putting several electrodes in parallel, and there is no reason why the power factor should be reduced.

Therefore as regards the type of furnace having a conducting hearth the whole practical question is as to the design of the hearth. If the construction of this hearth is such that its electrical conductivity is assured and that its preservation is perfectly feasible, the problem is solved, and this type of furnace may be adopted equally well for a unit of large capacity as for one of small capacity.

It remains then to determine in a practical way if the method in which the electric current flows in the steel bath forms a real metallurgical advantage. If this is so, the furnace with the conducting hearth has a determining factor of preference over the furnace with electrodes in series.

I propose eventually to return to this subject, which I have studied by working the two types of furnaces together.

As regards the furnace with electrodes in series I give further on information as to my experience and the results which I have obtained.

Part II.

Practical Working of Electric Steel Furnaces.

Furnaces With Electrodes in Series:

After a series of sundry industrial tests I patented in France[6] and in certain other countries, a furnace with vertical electrodes for entry and exit of the current, combined with a view to obtaining products by the "tapping" method; the characteristic of this furnace being the separate regulation of the two arcs created respectively at each electrode; that is to say, the realization in a furnace designed to tap the products obtained, of operating two separate heating zones at the upper surface of a conductive mass completing the circuit between the two electrodes.

Until 1902 I experimented with this furnace at the Kerrousse Works (Morbihan, France), for various applications, and notably for the manufacture of steel, when starting up with cold charges. I had available at Kerrousse a furnace tapping 1,750 pounds, permitting me to make steel ingots, which were tested at various places.

[6] French Patent, Ch. A. Keller, No. 300,630, May 23, 1900.

The lamented Ch. Bertolus, of Saint Etienne, visited this installation, and made it the object of a communication to the "Congress de la Houille Blanche," in 1902. Mr. Bertolus had previously made tests of the steel ingots from Kerrousse, at several steel works in the neighborhood of Saint Etienne, and published the results of the tests made at one of these works.[7]

The results of these tests, which owing to their early date possess to-day a certain interest from the chronological point of view, of the manufacture of electric furnace steels, showed that even then, by reason of the purification possible, the electric furnace imparted exceptional qualities to the steel, when starting with nondescript scrap.

Following these tests, which, of course, will be found very incomplete, now that the question has been actively elaborated in many places, I installed at the works of the Société des Etablissements Keller Leleux, at Livet (Isère, France), a two-electrode furnace tapping 5,500 pounds.

[7] Results of tests made at a Loire steel works upon a regular steel ingot from the Kerrousse Works, 1902:

Working of the metal: The metal was worked in its natural state, *i. e.,* just as received and without any tempering. It behaved perfectly under the drop hammer; and forged easily at a temperature of about 900° C. It bent well, was very soft, and worked with remarkable ease.

A part of the ingot having been pressed and hammered, without showing any fault, a strip 5 to 6 mm. thick and about 120 mm. wide was punched at red heat, close to its ends, with punches of different diameters; at the fourth test the metal had become very thin around the holes but had not broken or shown any alteration.

This same part of the ingot was cut into two parts, showing a very healthy appearance, denoting good steel.

Another piece brought to a temperature of 1250 to 1300° C., showed that the metal would not stand this heat, it would not work at that temperature. 1000° was a little too high, and above that it burned.

Mechanical tests: The ingot having been reheated to 900° a piece 80 x 80 mm. was forged with a drop hammer into a round bar for tensile tests, the bar being 500 mm. long and 30 to 32 mm. diameter. This was done very easily and with but one heating, showing that the metal is remarkably ductile.

Up to this time it might be supposed that the metal was a soft steel, but this test showed the contrary. The metal slowly cooled during this operation, when it was found that it possessed the very curious property, perhaps peculiar to itself, of becoming exceedingly hard about 500°, while it worked with great facility between 600 and 650°.

To test its hardness an effort was made to cut while cold a small piece from the tensile test bar, but the tool was dulled without cutting the piece very deeply so that to detach the pieces it was necessary to reheat.

Drill tests upon the same piece confirmed the hardness.

Bending and rebending tests made hot upon the prepared strips, and various thicknesses and widths, gave very good results; it was bent under the hammer, and straightened without showing any traces of fatigue.

Similar tests made transversely upon the metal gave equally good results.

These two tests showed that the metal had plenty of spring, which would lead one to suppose that the elastic limit would be quite high.

Here follows the note of the chief of tests, indicating the results as to tensile strength and elongation upon a test piece heated to about 900°, the test piece having been drawn out by hammering, and annealed before turning:

Diameter of test piece	13.8	mm.
Length	100	mm.
Tensile strength, per square inch	116,000	lbs.
Elongation	13	pct.

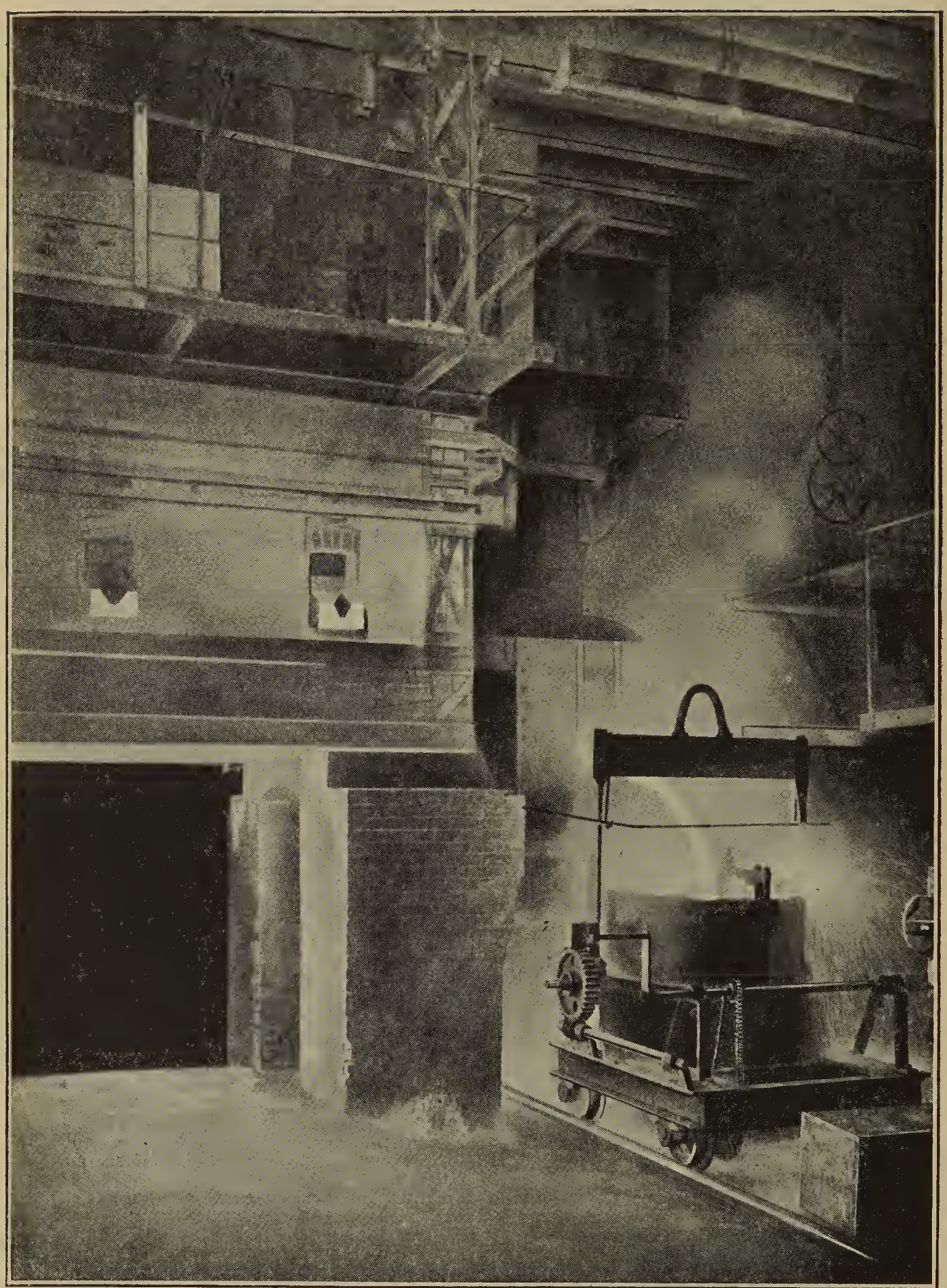


FIG. 9.—Keller Duplex System, Upper and Lower Furnaces.

This furnace was experimented with from 1902 to 1905, with the collaboration, from the metallurgical side, of Messrs. J. Holtzer & Co. of the Unieux Steel Works (Loire, France).

In 1905, following the results obtained at Livet, the installation of an electric furnace of 8 to 10 tons capacity, at the Unieux Works was decided upon.

This was the first electric furnace adopted in France by a steel works. It was and probably still is the most important electric furnace put into operation.

Ch. A. Keller Electric Furnace, Installed at the Steel Works of J. Holtzer, Unieux, France.

In the course of the electrometallurgical campaign started at Livet, I was able to satisfy myself that the electric furnace already had a place in the present day steel works, even if electric energy could not be obtained from hydraulic motors; but upon condition that the use of the electric furnace should be confined to reheating, mixing, deoxidation and purification of steel.

So as early as 1902 I patented[8] a method of dividing the manufacture of steel into two phases, confining to a special electric furnace the operations above indicated.

Liquid steel as obtained by the ordinary methods not being available, as the Livet Works did not have metallurgical furnaces for making steel, I installed two electric furnaces, one superposed above the other; the upper furnace serving for the oxidizing fusion of iron and steel scrap, the second taking the liquid steel to be finished. (Fig. 9).

I was thus able to determine the quantities of energy useful for each operation, and the scheme adopted for the Unieux installation arose from this series of experiments. The Messrs. Holtzer were the first metallurgists who decided to commence the construction of a complete electro-metallurgical installation, intended for the finishing in an electric furnace of previously melted and refined steel. The necessary energy for this installation is furnished by a steam plant. (Fig. 10).

The electric furnace of the J. Holtzer Steel Works is of the type with four vertical movable electrodes for carrying the current. Each electrode forms at its base a heating zone in which

[8] French Patent, Ch. A. Keller, No. 329,013, February 2, 1903.

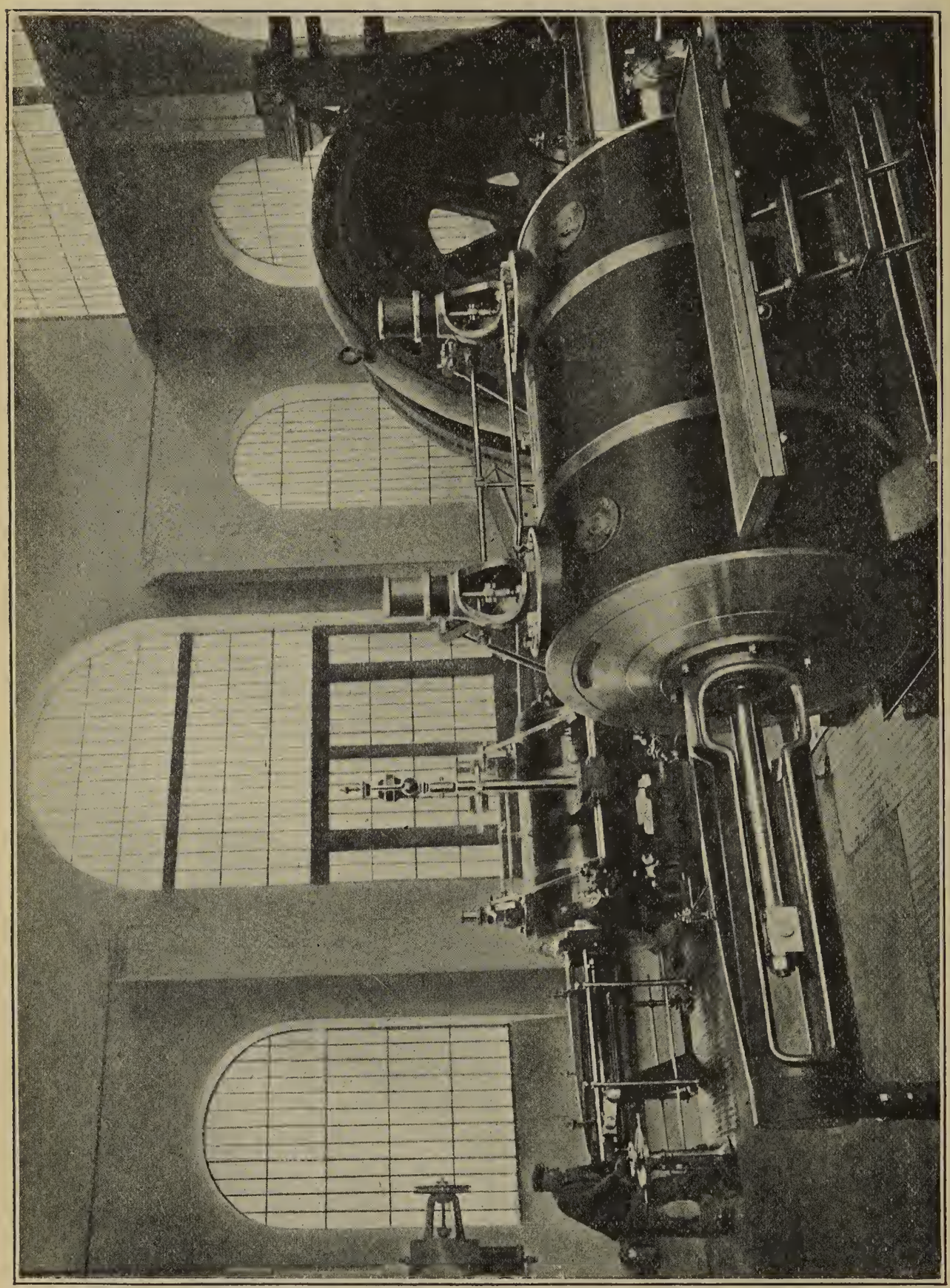


FIG. 10.—Steam Plant at Unieux.

the temperature can be regulated. Each pole carries two electrodes in parallel.

The construction of this furnace includes four principal groups or parts (Figs. 11, 12, 13, 14, 15, 16, 17).

(a) The movable furnace body, simply a metallurgical vessel without any electrical connection whatever, with its support, and suitable hydraulic movement.

(b) The revolvable electrode supports, with means for suspending the electrodes, and making electrical connection to a central block or head for distribution of electric current. These supports are completely independent of the furnace body, and when they are all turned outward the cover of the furnace may be easily lifted or removed.

(c) The overhead system of bus bars for distribution of current, having laterals so fixed as to engage connectors movable with the revolvable electrode carriers.

(d) The control board for the electrodes, with suitable valves for distant control, and the measuring instruments.

The movement of the electrodes is accomplished by means of hydraulic motors; the following combinations can be made:

Simultaneous raising of two electrodes of the same polarity or of the four electrodes together.

Simultaneous raising of two electrodes of the same polarity, and simultaneous lowering of two electrodes on the other pole.

Raising of one electrode and simultaneous lowering of the other electrode of same polarity.

Separate movement of any electrode.

The regulation of the electric circuits is obtained very simply in the following manner:

1. *Regulation of Voltage:* For voltage regulation the two electrodes of same polarity are moved simultaneously; if there is simply an inequality of voltage between the two poles, the two electrodes on each pole are simultaneously moved up and down with respect to each other. Thus by a single manœuver the balancing of voltage is accomplished. These combinations for manœuvering the electrodes are very simply realized by a suitable arrangement of gears commanding the valves of the hydraulic motors.

2. *Regulation of Amperage:* The amperage is equally divided

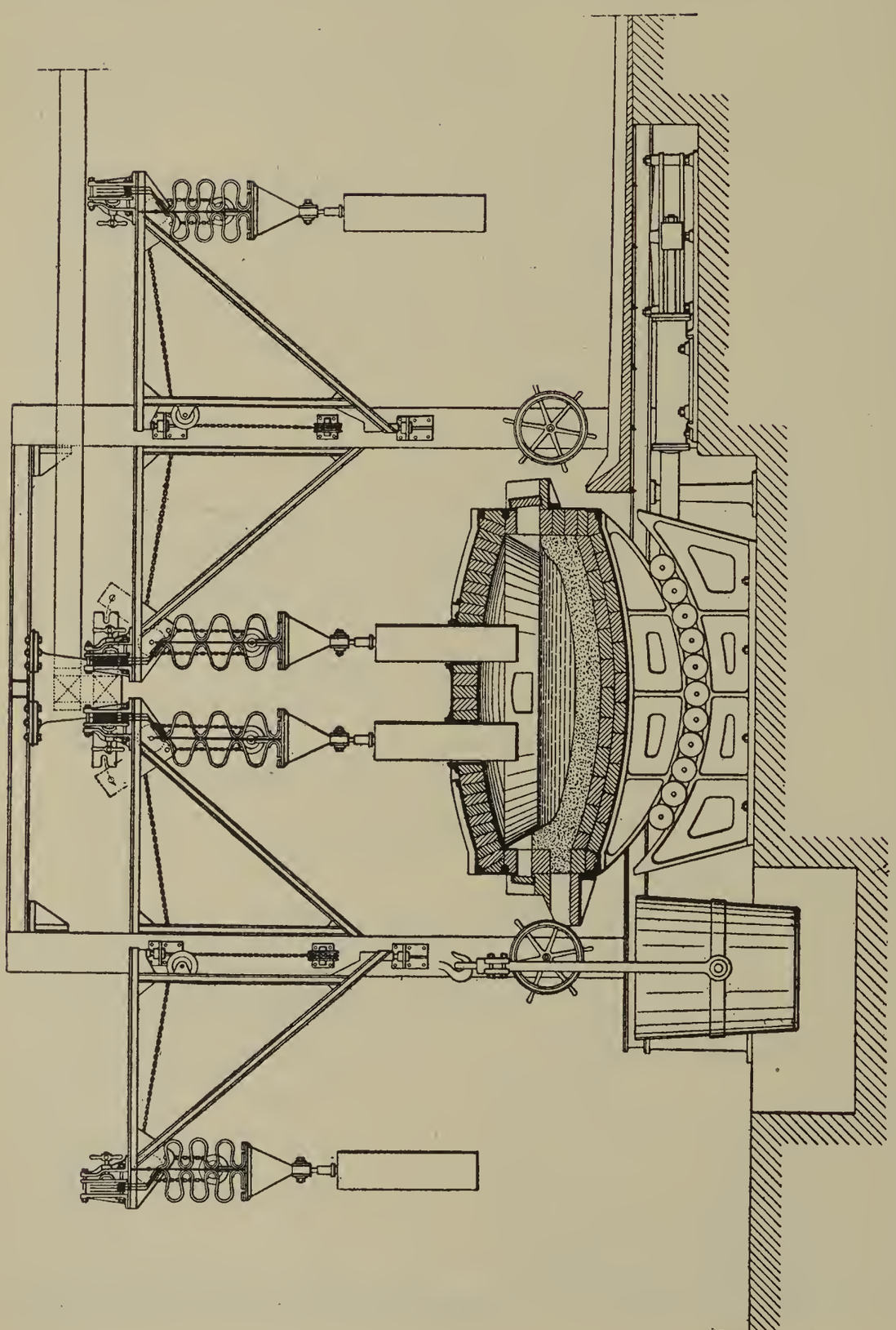


FIG. 11.—Keller Furnace at Holtzer Works, Unieux, France.

between the four electrodes by means of their separate movement; if there is simply an inequality of amperage between two electrodes of the same polarity, there is a simultaneous and inverse movement of these two electrodes. Thus also by a single manœuver the amperage is balanced between the electrodes.

This method of regulation by balancing of the voltage or amperage of one group of electrodes with the other, or of one electrode with the other of the same group, permits the use of a very simple and rational control apparatus.

I have applied, for the distribution of current to the furnace, an arrangement which I have called "Radiating Electrical Distribution" (distribution électrique rayonnante)[9] which enables me to reduce the self-induction to the lowest possible limit.

As I said before, the two electrodes of same polarity are in parallel. The total current is brought directly over the center of the furnace, above all its mechanical parts, by a system of interlaced copper bus-bars, connected to a central block firmly held by the metallic supports of the framework of the furnace. From this block four electric circuits radiate, each carrying two connectors for each electrode; one of these connectors is always idle. (Fig. 13 and 14).

The eight terminals thus formed are placed in electrical connection by suitable bent copper bars, with the main bus-bar system, the latter having ten bars each 10″ wide and 0.2″ thick, per pole.

The electrodes are suspended at the end of jointed arms which carry fittings for engaging the bus-bar terminals, thus connecting the electrode circuit with the bus-bar system.

The mode of distribution employed has the important advantage that it permits the replacing of an electrode while the furnace is running. The method of construction described also reduces to several minutes the time needed for replacing an electrode. Metallurgical operations may, therefore, be carried on without any interruptions due to handling of the electrodes.

When the rotating arms carrying the electrodes are turned outwardly (Figs. 12 and 15) the furnace body is entirely free of overhead encumbrances. The central connection block, which is placed high and out of the way, does not interfere with the

[9] French Patent, Ch. A. Keller, April 28, 1908.

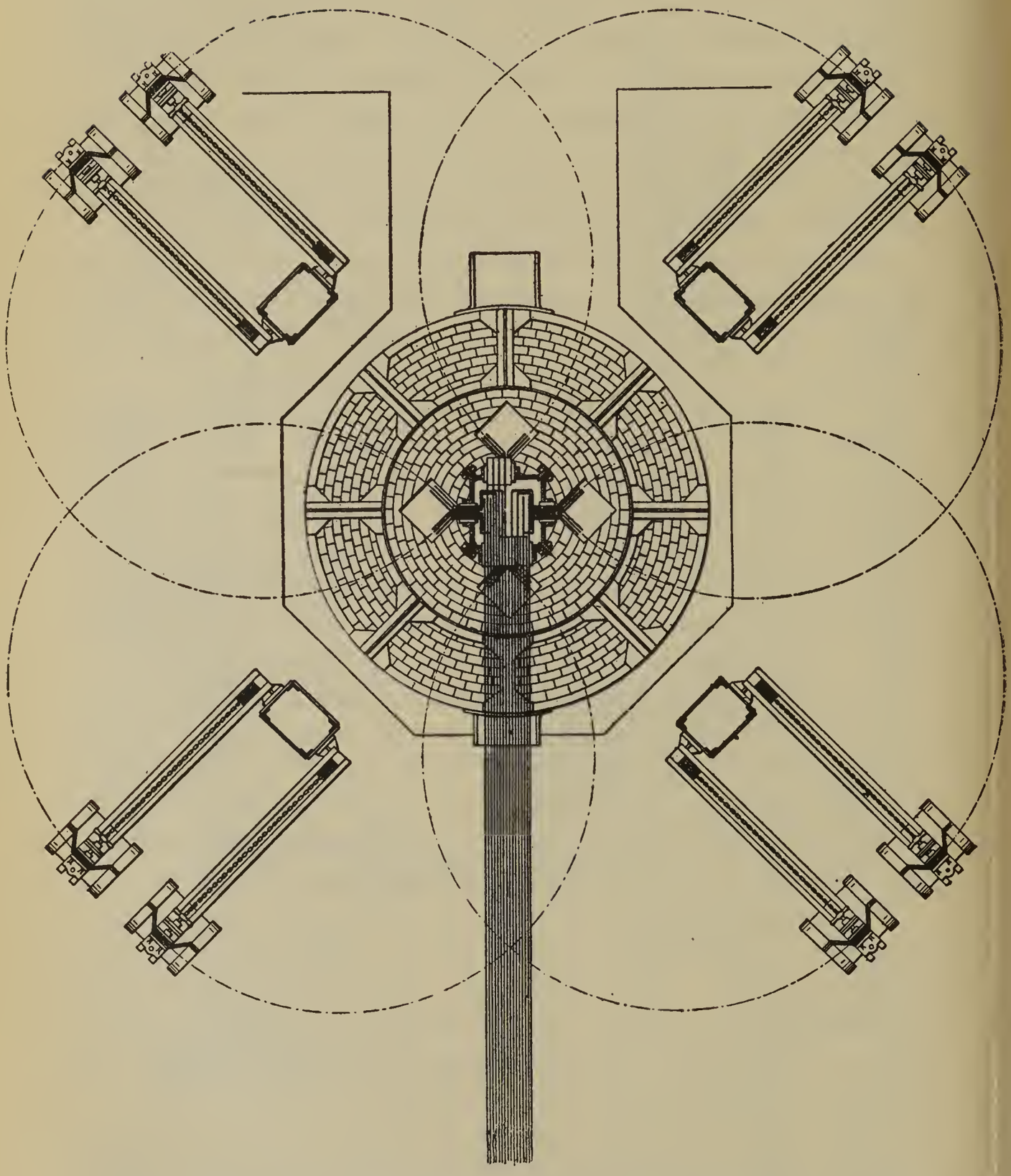


FIG. 12.—Plan of Electrode Holders and Connections, Keller Furnace at Unieux.

lifting of the cover, the latter being rapidly done by means of the traveling crane which passes over the furnace. In this way any cover requiring repairs may be easily replaced by a spare one; furthermore, the cover being lifted, repairs to the chamber itself are very easily made.

The overhead central bus-bar system with radiating branches placed directly above the electrodes, gives such low self induction that tests made at the J. Holtzer Steel Works have shown that the value of cos φ was about 0.97 with a current of 12,000 amperes. Consequently this disposition easily permits of the use of heavy currents, under very favorable conditions, and without fear of any serious lowering of the power factor.

The incumbrances above the furnace are much diminished by the use of a special fitting for the electrical connection between the electrodes and the overhead fixed terminals. It is recognized that the means of carrying the current between these parts should have a certain flexibility to permit of lowering and raising the electrodes.

To avoid every chance possible of short circuits between the two poles in the movement of electrodes, and in view of the close proximity of the electrodes, I have adopted the following arrangement.[10]

Very thin flexible bars, of ½ mm. thickness for example, are attached at one end to the fixed conductors which engage the bus-bar terminal and at the other with the electrode support. These flexible bars are divided into two sets, expanded and brought together again at several points in their length, where they are securely fastened. There is thus formed a series of flexible loops which contract and enlarge according to the position of the electrode. Where the bars are fastened together to complete each circle, they are fitted with small rings which slide up and down on cylindrical rods, thus acting as a guide.

This method of fitting produces a supple connection between the bus-bar terminals and the electrodes without introducing any overhanging protuberances larger than the natural transverse section of the electrode, thus leaving the space between the electrodes entirely free.

The four electrodes entering into the working chamber of

[10] French Patent, Ch. A. Keller, No. 387,462, May 6, 1907.

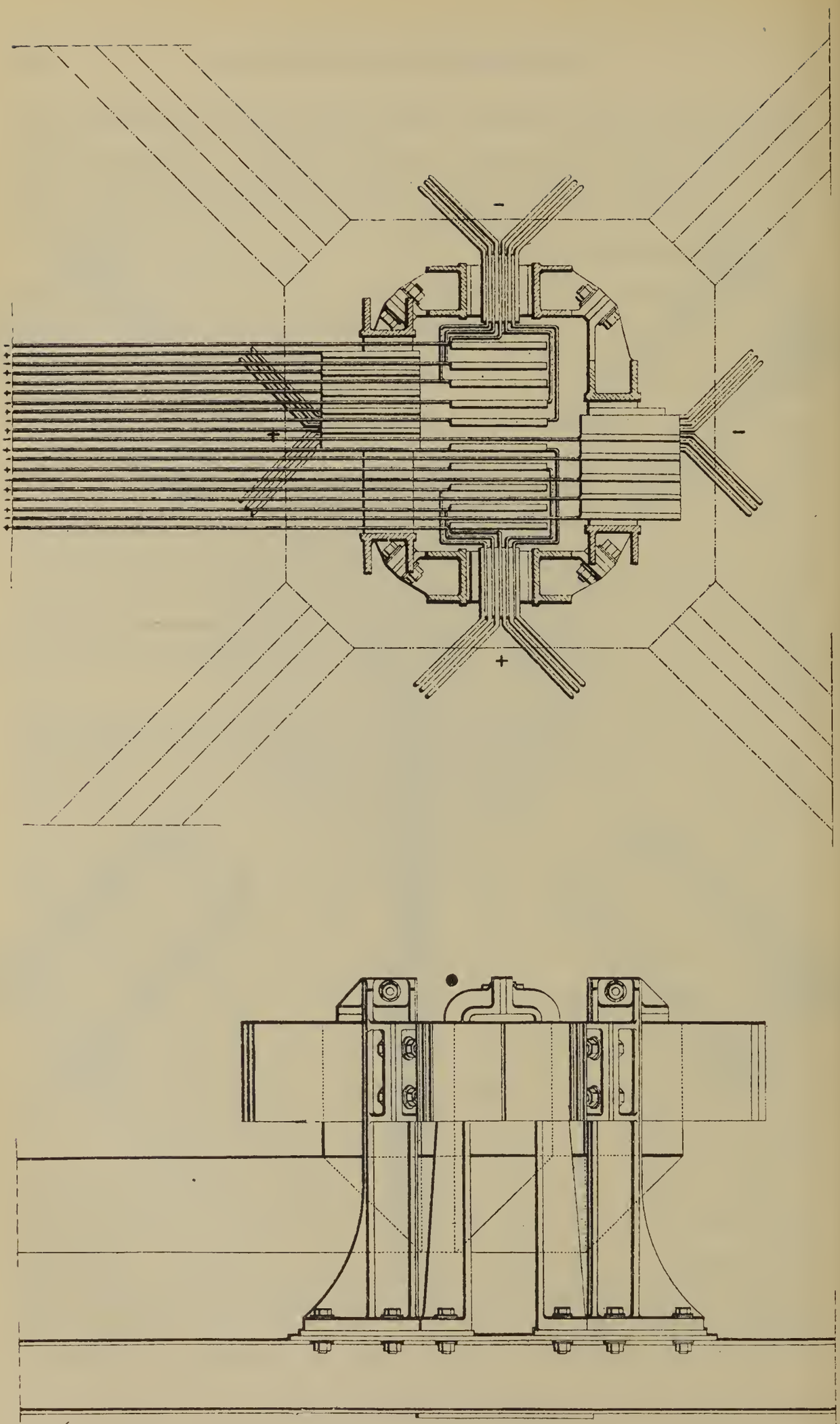


Fig. 13.—Bus-Bar System, Keller Furnace at Unieux.

the furnace pass through an arched roof covering the furnace.[11] The vessel containing the steel is circular in form, lined with magnesite. The furnace body is supported on heavy steel runners, working on rollers, by which it may be tilted as desired.

The tilting of the furnace may be in either the forward or backward sense, for tapping the steel or the slags; this is done by means of hydraulic cylinders.

The furnace body is fitted with openings in its circumference, for charging or watching the metallurgical operations.

During working the gases generated in the interior of the chamber create a slight pressure; this condition is imperative to avoid all entrance of air which would be prejudicial to the deoxidizing conditions wanted. The gases and vapors from the inter-

[11] I have experimented with and put into practice upon the large scale at the Livet Works an improvement in electric furnaces with electrodes in series (Fig. 18); this improvement consists in placing each electrode or each series of electrodes of different polarity in a separate chamber (French Patent, Ch. A. Keller, No. 336,403, November 2, 1903). The two capacities thus created were joined at the bottom by a canal filled with the metal being treated and which might exist there, according to circumstances, in either the solid, pasty or liquid state. When the metal in the canal exists in the solidified state, we have a furnace having a lateral metallic pole very

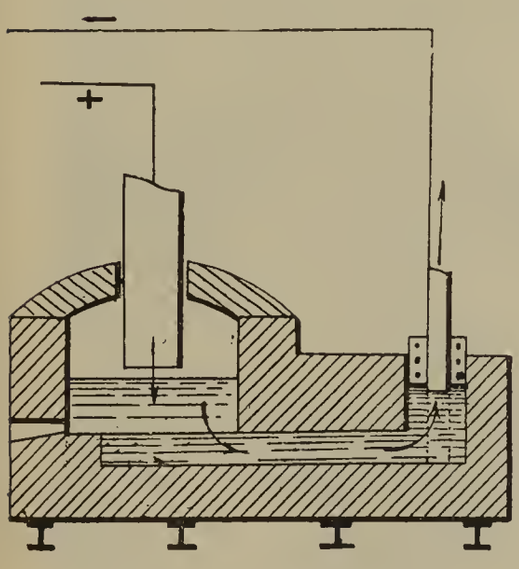


Fig. 19.

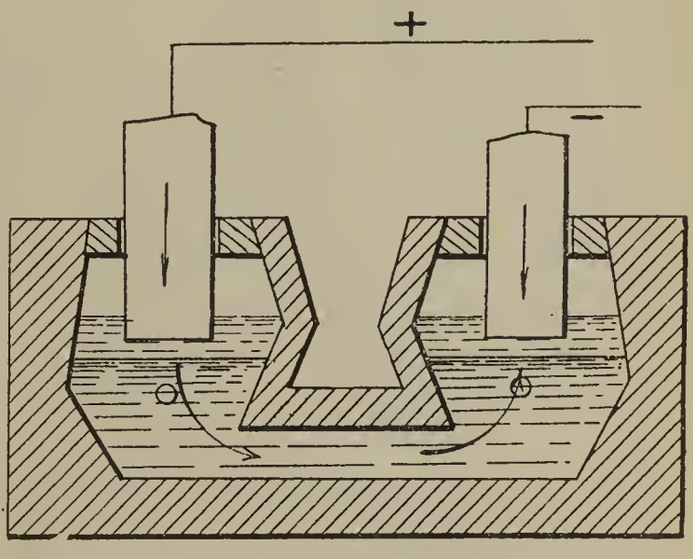


Fig. 18.

close in type to the furnace with conducting bottom previously described, and particularly to the furnace shown in Fig. 6.

The placing of electrodes of differing polarity in separate chambers has the advantage of producing a furnace in which the electric current passes through the entire depth of the fused metal. Further there is a benefit in construction resulting from having both poles formed by superposed electrodes.

If in a furnace of the above described type the electrode in one of the chambers is lowered until it touches the metal contained therein, this hearth is therefore in short circuit, and by this fact, the energy absorbed becomes nil. This variation in the method of operation of furnaces having separate chambers connected by a canal underneath, has been used by Mr. Chaplet and the Societe la Néo-Métallurgie (French Patent, Chaplet and Néo-Métallurgie, No. 270,005, September 25, 1906), for the construction of steel furnaces used at the Allevard Steel Works, in Isere. (Fig 19.)

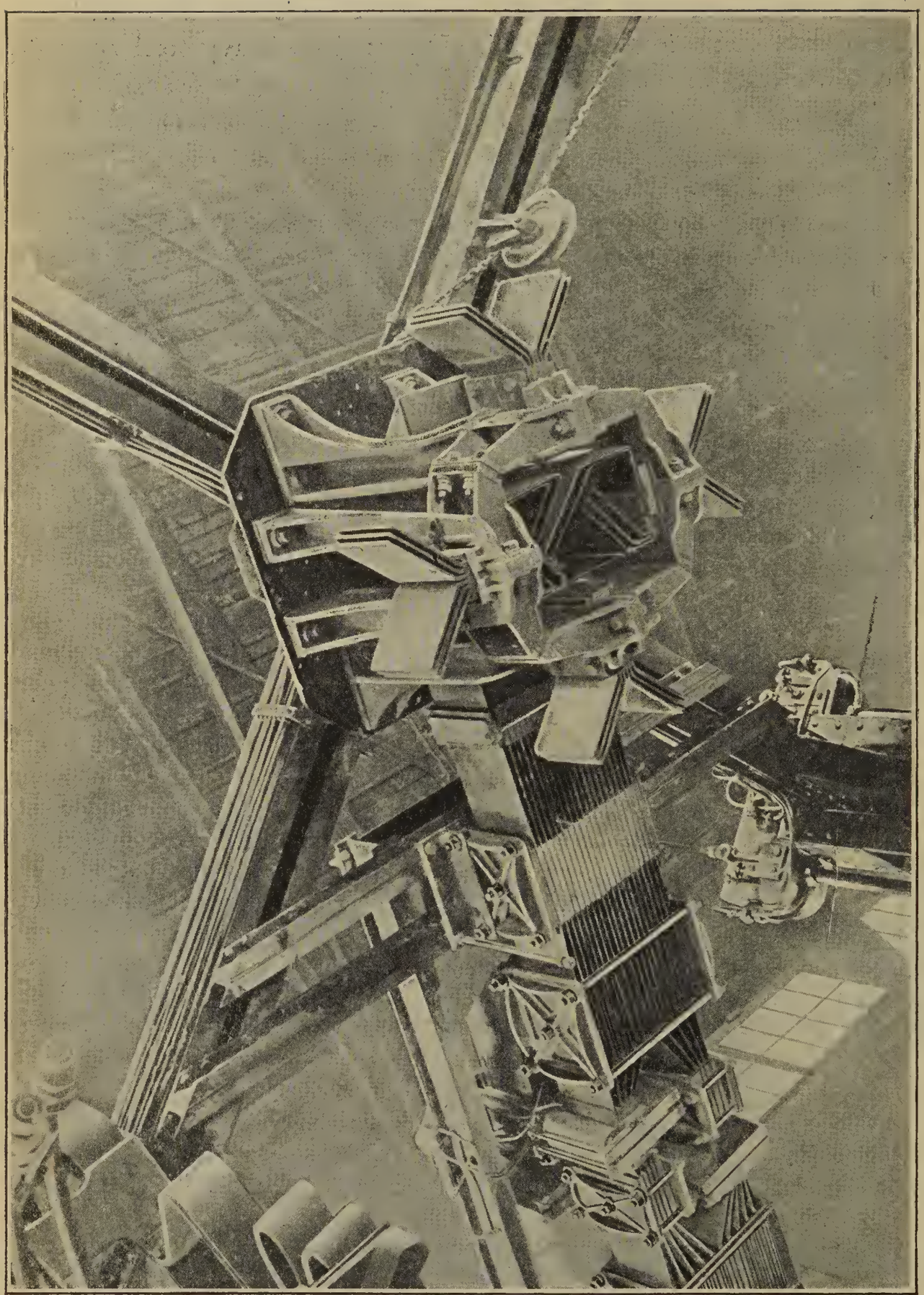


FIG. 14.—View from Beneath, of Electrode Holders, and Bus-Bar System.

ior of the furnace pass out through a pipe connected therewith, and into a chimney having an adjustable draft.

Results of Working of the Electric Furnace at the J. Holtzer Steel Plant.

At Unieux, steel is melted in a Martin furnace, then poured into a ladle which is immediately emptied into the electric furnace. The molten steel is thus put in circuit and the operations of deoxidation, additional refining and adjustment of chemical composition carried out.

The refining may be carried to 0.010 per cent. sulphur and phosphorus, while in regular practice 0.015 to 0.020 is attained.

The period of treatment varies of course with the quality of steel desired. As an example of regular practice, there may be quoted the following results abstracted officially and checked:

Weight of charge put into electric furnace...7,500 kgs.
Mean energy generation during operation.... 750 kw.
Period of working.....2 hours 45 minutes

Composition of molten charge:

C .....0.15 per cent.
S .....0.06 per cent.
P .....0.007 per cent.
Carbon content sought.....0.45 to 0.50 per cent.

Analysis of product:

C .....0.443 per cent.
S .....0.009 per cent.
P .....0.008 per cent.

Energy consumed per ton, 275 kw. hours.

Electrode consumption 18 mm. per hour for four electrodes having a cross-section of 400 x 400 mm.

For continuous working and assuming the cost of electrodes to be 35 francs per 100 kgs. this corresponds to a cost of about 4 francs (80 cents) per ton of steel.

The labor on the furnace, including feeding of the necessary materials, was provided by three laborers and one melter.

The regulation was manual and attended to by one of the three laborers, who looked after the repair of the furnace and the electrode connections.

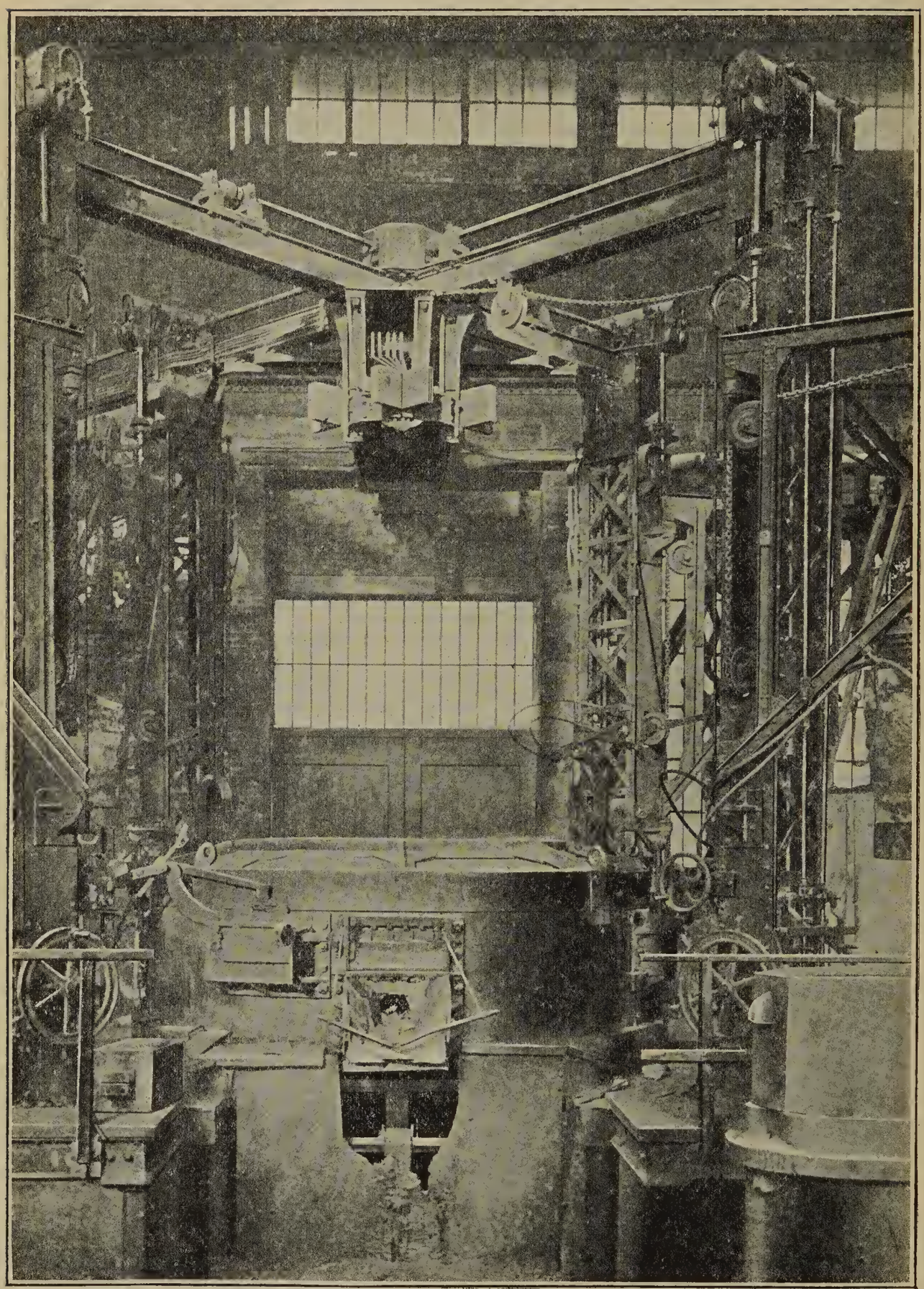


FIG. 15.—View of Furnace Dismantled.

The regulation could be carried on just as well by automatic regulators, but the regular behavior of the furnace, due to the existence of two parallel hearths for each pole, made automatic regulation by no means indispensable.

As another result of the metallurgical work of the Unieux furnace, I will quote for example a heat made for the production of 1,000 kgs. of ingots ordered from the Unieux works by a foreign steel works. It required the manufacture of a steel of armor plate quality.

The analysis of the steel supplied was as follows:

C	0.30	per cent.
Si	0.20	per cent.
Mn	0.56	per cent.
S	0.007	per cent.
P	0.013	per cent.

The steel contained besides a certain quantity of nickel. The acceptance tests on these ingots were made on plates 36 mm. thick rolled to a width of 325 mm.

The test pieces, 13.8 mm. in diameter and 100 mm. between marks, gave the following results:

TABLE I

	Elastic Limit. lbs. per sq. in.	Ultimate Strength. lbs. per sq. in.	Elongation. per cent.	D/d
1 (longitudinal)	86,300	112,000	17.0	5.3
2 "	86,300	113,000	16.5	4.8
1 (transverse)	86,300	112,000	14.0	3.3
2 "	88,000	112,500	14.0	3.4

[*Note:* Apparently the "longitudinal" test means that the test piece was cut out with its longest dimension in the direction of rolling, while the transverse test piece was cut with its longest dimension perpendicular to the direction of rolling.—Trans.]

DROP TEST ON UN-NOTCHED SPECIMENS:

Longitudinal specimen:

Deflection at 15th blow	24 mm.
Angle of rupture	30°
Fracture	Long fibers

Transverse specimen:

Deflection at 15th blow	24 mm.
Angle of rupture	86°
Fracture	Short fibers

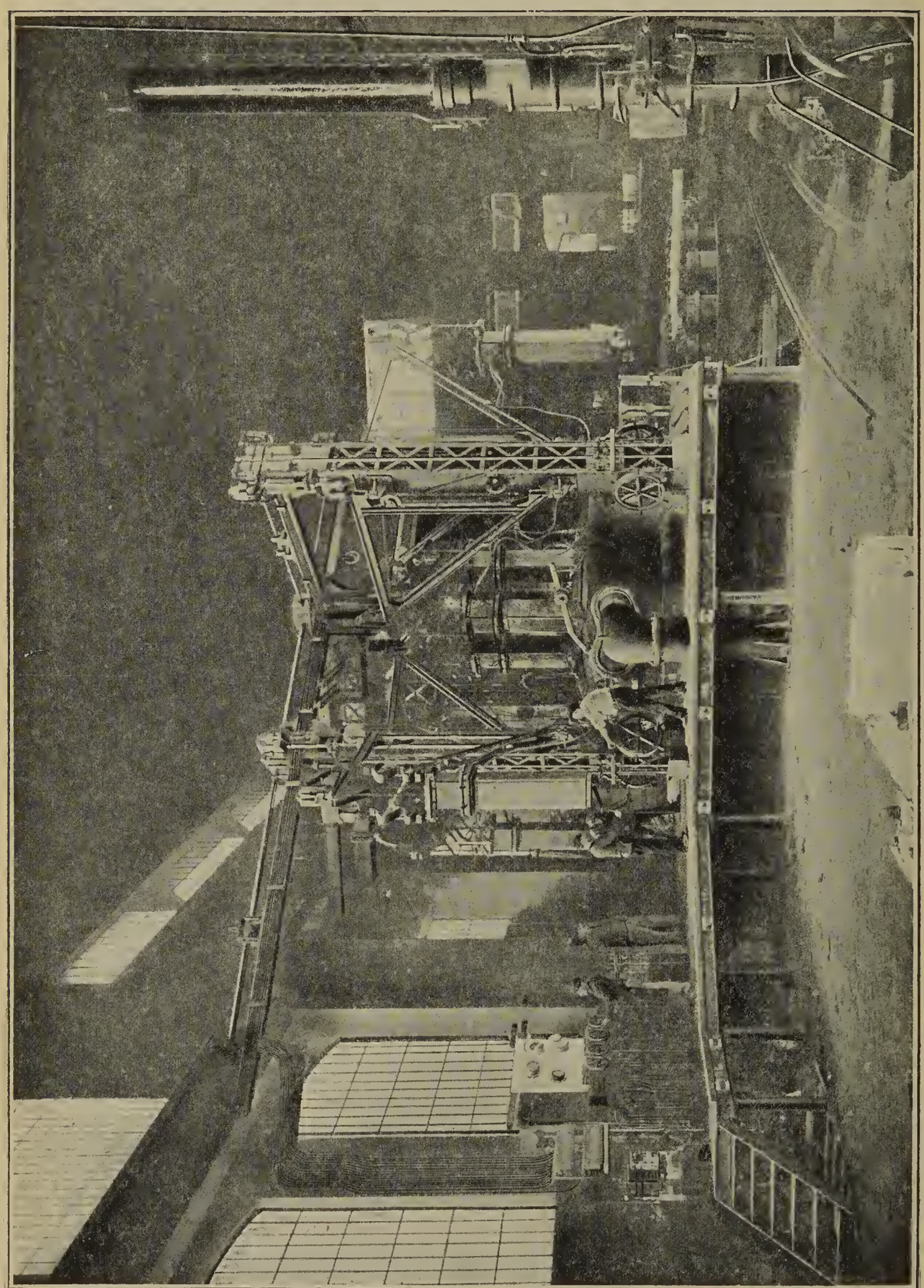


FIG. 16.—Furnace Ready for Operation.

DROP TEST ON NOTCHED SPECIMENS:

Longitudinal specimen:

Ruptured at 7th blow
Angle of rupture.....147°
Fracture .....wholly fibrous

Transverse specimen:

Ruptured at 4th blow
Angle of rupture .....158°
Fracture .....Fibrous

The drop-tests were made on bars 30 x 30 mm. with the following conditions:

Un-notched bars:

Distance of supports.....160 mm.
Weight ..... 18 kgs.
Height of drop.....2.75 meters

Notched bars:

Distance of supports.....100 mm.
Weight ..... 18 kgs.
Height of drop.....1.50 meters

The treatment of the metal consisted of two temperings in water at a clear cherry red on the unwrought, rolled and annealed plates.

The qualities of these steels, both from the point of view of purity and that of various mechanical tests, are a proof that the electrode furnace forms a metallurgical apparatus in every sense of the term; a flexible apparatus which permits of precise metallurgical work; a new metallurgy, not because of the absolute material results obtained (for up to the present the quality and purity of the best crucible steels have never been surpassed), but because of the method used, which differs in no respect from that governing the operation of the Martin-Siemens' furnace, perfected by new results procured by the high temperature and the neutral atmosphere due to the employment of an electric source of heat.

I do not desire here to draw a parallel between the furnace without electrodes and the electrode furnace. But I cannot do otherwise than express the opinion that if we consider the simple and extensive metallurgical facilities provided by using electrodes, and the small electrode consumption per ton of steel, we are led to ask how it can be argued that elimination of electrodes

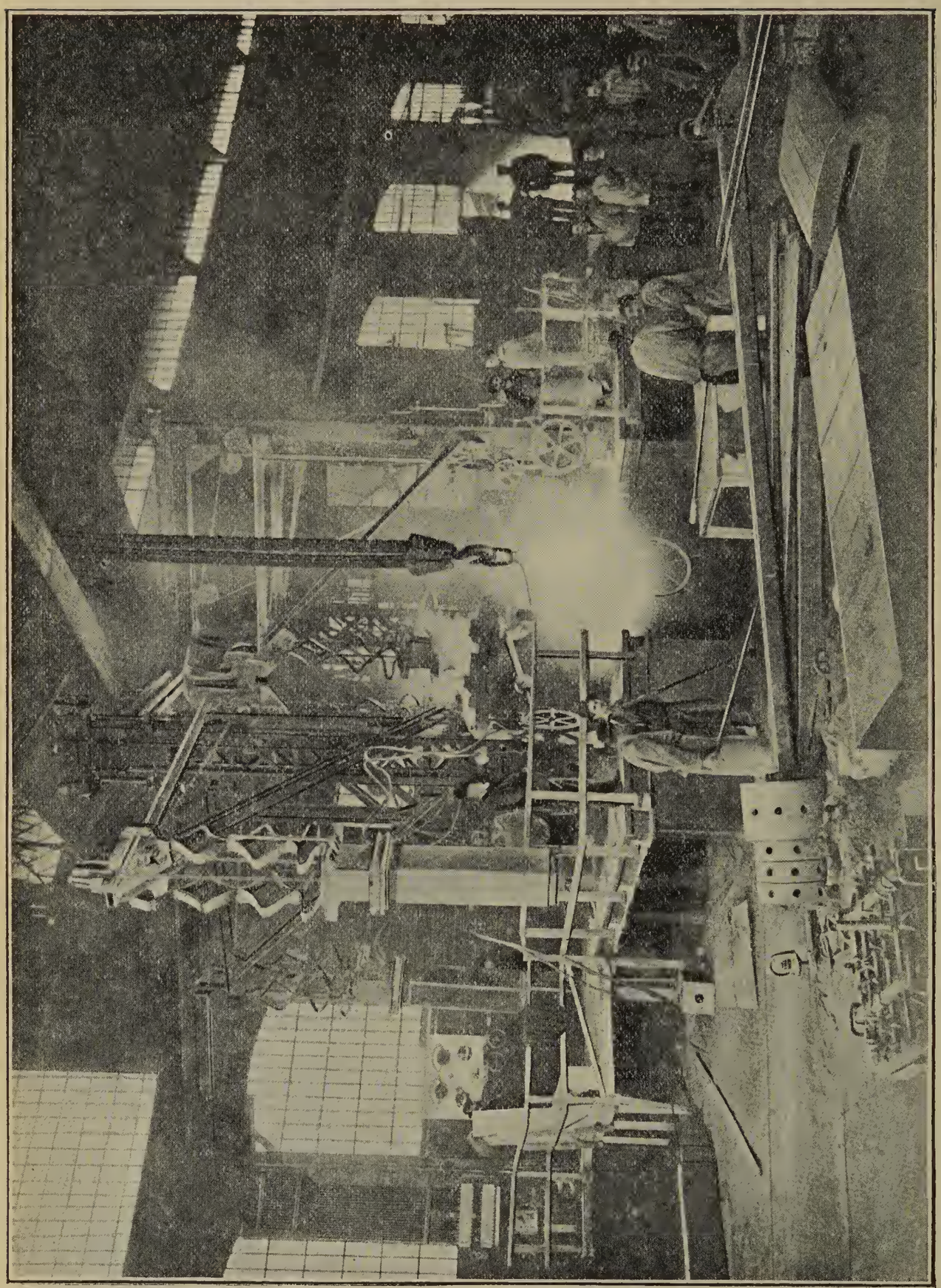


FIG. 17.—Tapping the Keller Furnace at Unieux.

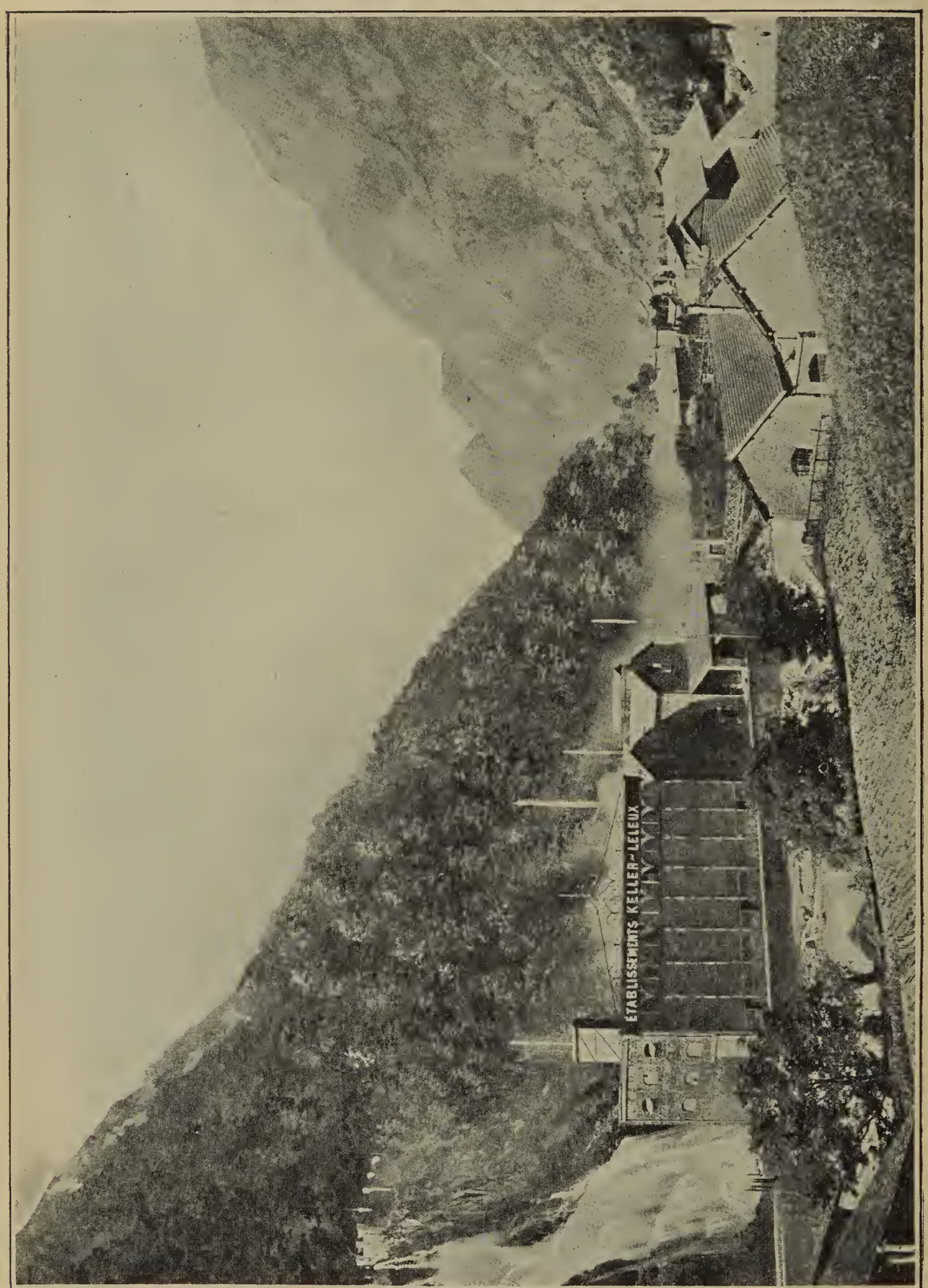
(and a loss of some of the advantages which they possess) can constitute a determining factor in the adoption of a furnace without electrodes in preference to an electrode furnace.

Again it must be added that the construction of electrode furnaces is very simple, and that the electrical equipment which supplies them belongs to ordinary everyday electric construction, that the furnaces without electrodes are of complex construction and that they cannot, as it seems to me, be left without hesitation to the ordinary workman.

The electrode furnace should find its principal place in metallurgy in the direct application of three-phase currents, for many steel works already have central stations supplying three-phase current. Finally, at the present day the transport of energy is generally installed in the form of three-phase current, therefore, it is necessary to consider the use of this form of current in order to fill the demands of most cases which are presented.

These considerations have led me to a study of a three-phase furnace for the manufacture of steel. This furnace may be worked with electrodes in delta or star connection. In the first case each of the three electrodes is connected respectively with each phase of the circuit, in the second case the electrically reinforced bottom of the furnace, which I have described, is connected to the neutral point of the three-phase system.

The three-phase electric furnace combines to a great extent the qualities of furnaces with electrodes in series and furnaces with conducting hearths if the connection is in star, for the steel is partly "electrified. It is now possible to approach without fear the construction of a three-phase furnace having a capacity of 20 tons; this furnace would necessitate the use of about 1,800 kilowatts; such a furnace would be capable of purifying 250 to 300 tons per day of ordinary steel from the Thomas converter in a series of heats which would last about 1½ hours each, and which would bring the sulphur content of the molten steel from the Thomas converter from 0.08 to 0.02 per cent. approximately, at the same time permitting of deoxidization and decarburization as required. The cost of work of this kind would vary from 15 to 20 francs per ton of steel treated, calculating electric energy at 0.015 francs (0.3 cent) per kilowatt hour, a price which may be reached with gas engines supplied from blast furnaces if no



Livet, Isère, France.

value is assigned to the gas, and estimating the other factors of cost at a price corresponding to their usual value.

The passage of steel through the electric furnace where, under the influence of superheating, it would be subjected immediately and rapidly to a marked desulphurization, would permit the use in the converter of pig iron higher in sulphur. This advantage would enable a metallurgical works, taking advantage of this circumstance, to use ores which otherwise would have been rejected, and thus the introduction of the electric furnace in such a factory would have a two-fold and important economic application.

The possibility of economically interpolating the electric furnace in the general cycle of great metallurgical operations should open a new era; that in which the employment of the so-called ordinary qualities of steel is gradually abandoned.

In giving to structural steel and rail steel additional qualities of safety, the electric furnace will contribute to the realization of a higher civilization, by diminishing in great part the probabilities of catastrophies due to defects in quality.

There can be no doubt that impelled by their traditional initiative and by the sense of the imperious necessity of always doing better, metallurgical works of the highest class will shortly take up the method of electro-siderurgy.

Nor is it to be doubted that great public or private authorities, conscious of the responsibility and obligation which humanitarian considerations above all impose upon them, will soon base their requirements as to steel on the new guarantees which the most recent progress of modern technology reveals to them through electro-siderurgy.

Livet, April 15, 1909.

A paper presented in abstract by Mr. L. E. Saunders, at the Fifteenth General Meeting of the American Electrochemical Society, at Niagara Falls, Canada, May 6, 1909; President E. G. Acheson in the Chair.

THE GIROD ELECTRIC FURNACE FOR THE MANUFACTURE OF STEEL.

By Paul Girod.

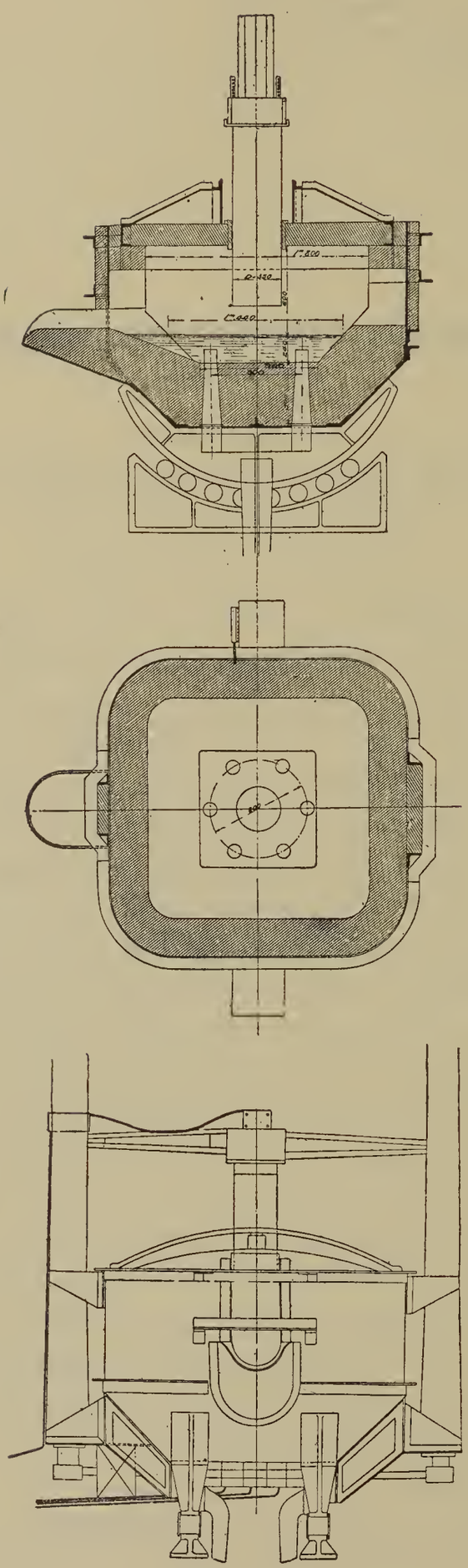
Managing Director of the Société Anonyme Electro-métallurgique, Procèdés Paul Girod, Ugine, France.

(Translated by P. McN. Bennie.)

The working portion, or hearth, of the Paul Girod Electric Furnace consists of a circular or oblong chamber, which when working is filled with molten metal to a depth of 25 to 30 cms. (12 to 14 inches). One or more electrodes of like polarity are suitably suspended above the bath; the other pole or terminal consists of a number of pieces of soft steel buried in the refractory material of the hearth at its periphery, the upper ends of which come into contact with the metallic bath. The circuit thus established, the electric current forms an arc between the upper electrode and the surface of the bath, through which it passes by the connecting pieces of soft steel to the other terminal of the furnace.

The upper portions of these connecting pieces directly in contact with the metallic bath naturally fuse to a certain depth, which does not, however, exceed 2 to 4 inches, as has been demonstrated by sections made of these pieces after several months' use. In order to decrease the depth of the fused portion as much as possible, and to assist in preserving the lower portion of the refractory lining of the furnace, the lower extremities of the connecting pieces are fitted with a water-cooling arrangement, in a cavity about 6 inches deep, in that portion of the steel connectors projecting outside of the furnace; this also serves for connecting the cable to this terminal.

According to the capacity of the furnace, one or more electrodes are used above the bath, but if more than one is used they



are always in parallel, connected to the same terminal of the generator or transformer, the other terminal being connected to the metallic connecting pieces.

The furnace may be run with either continuous or alternating current, but in the latter case it is necessary to take into account that cos. φ will be about 0.88.

The furnace body consists of a metallic shell of plate steel, forming a chamber round, square or rectangular, as may be desired, lined with suitable refractory material (magnesite or dolomite). The furnace is supplied with suitable charging and working doors and a tap-hole. The steel is tapped by tilting the furnace, for which purpose it may be mounted upon trunnions or rollers.

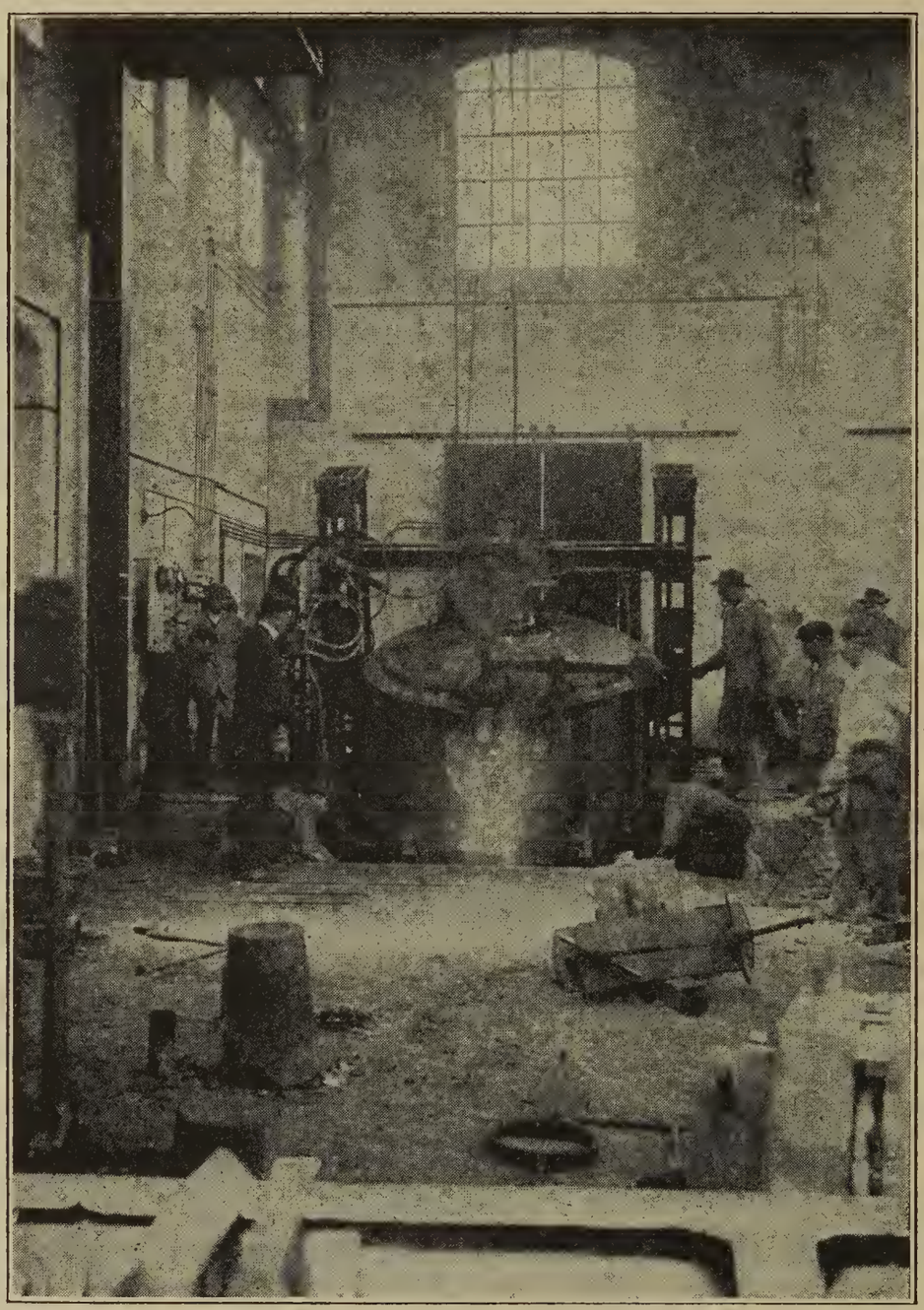
A cover lined with silica brick is mounted over the furnace, the ports for the electrodes being fitted with a removable cast-iron water-cooled frame.

The electrodes are so fitted that air cannot enter the furnace, this and the use of metallic frames or collars being possible by the fact that the electrodes have the same polarity, and there is, therefore, no danger of short circuits across the cover. The use of the metallic frames for the electrode ports is not altogether necessary, but has the advantage of more perfectly closing the furnace and stiffening the cover.

Advantages of the Paul Girod Furnace: The Paul Girod furnace may be classified in the category of arc furnaces, but it works also partially by resistance, due to the passing of the current through the metallic bath. This resistance feature becomes of prime importance in starting up a furnace with a charge of cold scrap, turnings or cast iron. The current passes through this mass of discrete particles so that almost the entire potential difference between the terminals of the furnace is absorbed by the high resistance of the charge, a great number of small arcs being formed between neighboring pieces. The heating and melting begins, therefore, throughout the entire mass of the charge simultaneously.

The great ease with which the furnace may be started up with cold charges is a marked advantage of the Girod furnace over other systems. The method of arranging the electric circuit permits of easy automatic regulation of the arc, as there is but one

drop of potential to be regulated in the circuit, instead of two successive drops, as is the case in furnaces having two electrodes in series. Like all arc furnaces, the Girod furnace lends itself extremely well to the work of refining the metal; it permits of

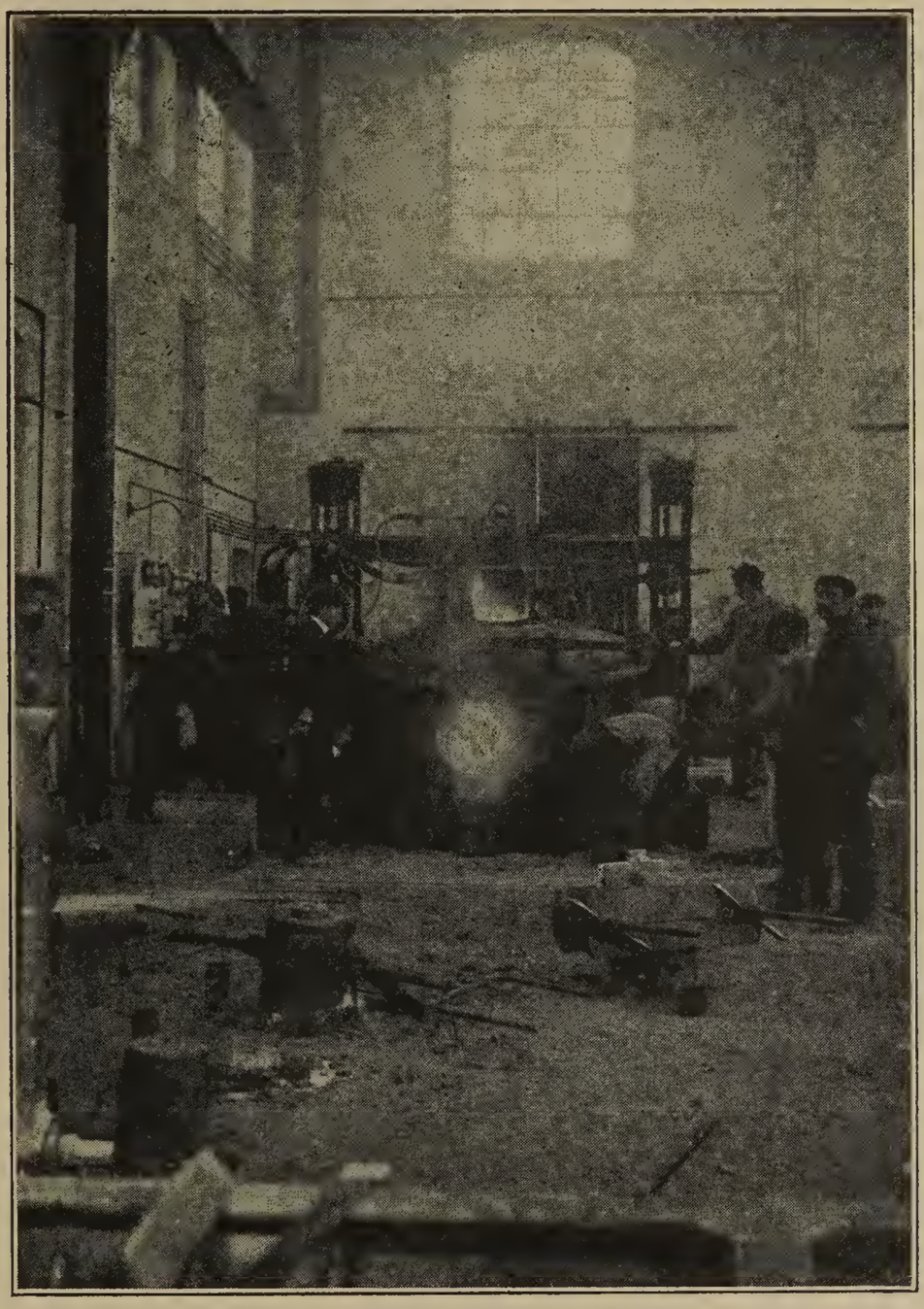


Girod Furnace.—Pouring Into a Large Suspended Ladle.

obtaining very hot and fluid slags, which may be entirely removed during the handling of a charge. The low voltage at which the furnace works (about 55 volts) makes it very easy to thoroughly insulate all parts of the furnace circuit, or any places where short circuits might occur; this is an additional safeguard for workmen

who may, by reason of their duties or accidentally, come in contact with the current.

Manufacture of Steel: The following data have been taken from Girod furnaces in actual operation at Ugine, in the works of the Compagnie des Forges et Aciéries Electriques Paul Girod.



Girod Furnace.—Pouring Into a Hand Ladle.

One of these furnaces has now been working for several years and has never given the slightest trouble which could be ascribed to its particular form or design.

Raw Materials: The raw materials at Ugine consist of scrap, turnings and some cast iron, gathered indiscriminately in the

market. The problem, therefore, is to refine these materials, charged cold, to obtain a high-grade steel; the furnace at Ugine should, therefore, be classified as of the Class III *"Production of steel from scrap materials when charged cold into the furnace."*

The average analysis of raw materials charged is as follows:

C	0.400 to 0.500
Si	0.150 to 0.250
Mn	0.500 to 0.700
S	0.060 to 0.090
P	0.080 to 0.100

Finished Products: The finished steels are of any desired grade, of all degrees of hardness, carbon and special structural steels, tool steels, cast steels, etc.

Analyses of some of the Ugine steels are given below:

TABLE I.

Grades of Steel Made at Girod's Works.

No.	Quality	C	Si	Mn	S	P	Cr	Ni
1	Extra soft	0.079	0.106	0.205	0.015	0.012		
2	Soft	0.236	0.180	0.431	0.012	0.010		
3	Medium	0.283	0.208	0.430	0.014	0.010		
4	Medium hard	0.388	0.155	0.342	0.011	0.009		
5	Medium hard	0.463	0.204	0.463	0.010	0.016		
6	Hard	0.595	0.198	0.302	0.017	0.005		
7	Nickel, 2%	0.076	0.099	0.101	0.014	0.010		2.12
8	Nickel 3% soft	0.06	0.125	0.209	0.013	0.007		3.47
9	Nickel 3% hard	0.364	0.144	0.435	0.012	0.015		3.41
10	Nickel 5% soft	0.134	0.148	0.375	0.016	0.013		5.25
11	Nickel 5% medium	0.25	0.157	0.414	0.010	0.015		5.08
12	Nickel chrome	0.420	0.199	0.500	0.010	0.009	0.77	2.53

TABLE II.

Tool Steels Made at Girod's Works.

C	Si	Mn	S	P	Cr	Ni	Wo
1.223	0.168	0.224	0.011	0.010			
1.474	0.119	0.264	0.015	0.007			
1.010	0.219	0.306	0.008	0.009	0.32		
1.277	0.230	0.130	0.009	0.006	0.24		
1.251	0.176	0.258	0.010	0.008	1.21	0.49	
0.689	0.029	0.096	0.012	0.009	6.07	0.46 (Mo)	25.82

Physical Tests: The characteristics of electric furnace steels are, compared to Bessemer, open-hearth or crucible steels, their high elastic limit, and their great resistance to shock. These

qualities seem due to the chemical purity of electric furnace steel, to its homogeneity and freedom from occluded gases. The two latter points are of greater importance, inasmuch as the sulphur and phosphorous content hardly ever exceeds 0.030 per cent. anyhow. In support of these claims, we give some results of mechanical tests made with Ugine steels.

TABLE III.

Mechanical Tests of Steel Made in Girod's Electrical Furnace.

No.	Treatment	Elastic Limit lbs. per sq. in.	Tensile Strength lbs. per sq. in.	Elongation. per cent.	Contraction. per cent.	Resilience Ft. lbs. per sq. inch
1	Annealed at 900° C.....	40,700	54,800	31.5	70.5	2,240
1	Hardened at 850° C.....					
	Tempered at 450° C.....	48,200	62,700	29.0	80.0	2,330
2	Annealed at 900°.....	51,100	72,400	24.5	60.0	1,680
2	Hardened at 850°.....					
	Tempered at 450°.....	65,700	97,200	17.0	74.0	1,490
3	Annealed at 900°.....	49,000	79,500	20.5	56.0	1,420
3	Hardened at 900°.....					
	Tempered at 450°.....	93,700	114,300	15.0	61.0	1,300
4	Annealed at 900°.....	58,200	88,000	10.0	51.0	745
4	Hardened at 900°.....					
	Tempered at 450°.....	95,800	113,600	13.5	57.0	725
5	Annealed at 900°.....	72,400	107,900	16.5	41.0	515
5	Oil hard. at 900°.....					
	Tempered at 450°.....	123,500	140,400	11.0	46.0	605
6	Annealed at 900°.....	69,600	121,400	12.5	16.5	490
6	Oil hard. at 900°.....					
	Tempered at 450°.....	103,700	142,700	10.0	35.7	560
7	Annealed at 850°.....	44,000	58,900	29.0	69.0	1,865
7	Hardened at 850°.....					
	Tempered at 450°.....	54,600	67,000	26.0	75.0	2,050
8	Annealed at 850°.....	46,100	61,000	29.0	69.0	1,515
8	Hardened at 850°.....					
	Tempered at 450°.....	70,000	80,900	20.0	72.0	1,305
9	Annealed at 850°.....	72,400	92,300	18.5	45.0	675
10	Annealed at 850°.....	55,380	72,400	23.5	63.0	1,775
	Buried in lime.....					
10	Hardened at 850°.....					
	Tempered at 450°.....	102,200	106,500	12.5	64.0	1,820
11	Annealed at 850°.....	95,100	105,000	13.5	55.0	1,305
	Air cooled					
12	Annealed at 800°.....	100,800	123,500	10.0	41.0	700
12	Oil hard. at 825°.....					
	Tempered at 450°..... ...	152,000	160,500	12.5	60.0	980

NOTE.—The tensile tests were made upon test pieces 13.8 mm. diameter (0.54 inches) and 4 inches between marks.

TRANSLATOR'S NOTE.—The resilience test, resistance to shock, or toughness, is given in kilogrammeters per square centimeter, determined with a Guillery falling weight apparatus upon bars 10 mm. square section, with a nick 2 mm. wide and 2 mm. deep. We have transposed this into foot pounds per square inch.

General Data as to Costs of Melting: The factors which enter into the cost of manufacture of steel in the Girod furnace are generally as follows, in the alternative of working with cold charges, with or without refining (Class III), or with molten charge (Class VI). The figures refer to the ton of steel produced.

(1) Treatment of a Charge of Cold Scrap, With Refining.

Energy Consumption: The average energy consumption for fusing, refining and finishing a charge of cold scrap is 900 kw. hours per ton of steel in a 2-ton furnace, and 700 kw. hours in a furnace holding 8 to 12 tons, the energy being measured at the furnace terminals. These figures will, of course, be slightly increased in the case of special steels, or diminished as the refining period is shortened.

Electrode Consumption: The electrode consumption is about 16 to 18 kgs. (35 to 40 pounds) in a 2-ton furnace, and 13 to 15 kgs. (29 to 33 pounds) in an 8 to 12-ton furnace per ton of steel produced. The unused portions of the electrodes, corresponding in length to the height of the arched cover above the bath, are included as having been actually consumed.

The consumption of electrodes will obviously depend upon their quality; that indicated above refers to ordinary amorphous carbon electrodes made from retort carbon, and not to graphitized electrodes.

Linings: The lining is of brick (or, better still, a paste) made of magnesite or dolomite. These materials give equally good results, and, therefore, the one is used which can be had at the lowest price. In France dolomite is generally used, as the price is very much lower than magnesite.

One such lining will last 40 to 50 heats without any repairs, after which the lateral walls of the furnace receive partial repairs. Now and then, generally after 100 heats, the upper portion of the hearth lining for a distance of about 10 cms. (4 inches) is repaired also; after having scraped and cleaned the hearth, magnesite or dolomite is rammed in for a height of about 10 cms., taking care to preserve the passage for the metallic contact pieces.

The hearth otherwise does not require any other repairs than

fixing up the sides for the distance of 10 cms. Thus in the oldest furnace in use at Ugine the same hearth has been in place for over two years without having needed repairs.

The cover is of silica or high-grade fire brick, the life depending upon the quality of the brick; with good material a cover will last through 40 to 50 heats. Under these conditions, in France, the expense for furnace linings will be 7 to 8 francs ($1.40 to $1.60) per ton of steel produced in a small furnace, and 4 to 5 francs ($0.80 to $1.00) in a large furnace of 8 to 12 tons capacity.

Labor: To handle the furnace three men are sufficient, a melter, an assistant melter and a boy, for small furnace; four men for a large furnace. At Ugine the large furnaces are charged by an electric charging machine.

Additions: To the expense above mentioned should be added the sundry additions, such as lime, ore and fluorspar, for the various slags, on one hand; and ferro-alloys, ferro-manganese, ferro-silicon, silico-manganese, etc., added during the final period and finishing of the metal, on the other hand. The total of these items will vary essentially with the purity of the prime materials used and with the quality of the steel to be made; it varies between 3 and 7 francs ($0.60 to $1.40) the ton.

Losses: The loss in the furnace will depend mostly upon the composition and state of oxidation of the scrap and materials charged; with heavy scrap but little oxidized, the loss is from 6 to 7 per cent.

(II) Treatment of a Charge of Cold Scrap, Without Refining.

This is the case where a charge of selected and sufficiently pure materials is simply melted in the electric furnace. The time of the heat is diminished by 25 per cent., so that the various expenses of melting, as above, are reduced to about 75 per cent. of their values in Case I.

(III) Treatment of a Charge of Liquid Steel.

The molten steel can be taken from a Bessemer converter, or from a Martin, or open-hearth furnace. The time of the heat is then reduced to 20 to 30 per cent. of the length of a heat of

material charged cold and refined (Case I). The various factors entering into the cost are brought to 20 to 30 per cent. of the values indicated in Case I. The energy consumption, the carbon consumption and repair costs of the furnace are very much reduced by the fact that the furnace is kept constantly hot, there being no important drops in temperature as in the case of cold charging—a condition unfavorable both from the point of view of energy consumption and preservation of linings. These results are drawn particularly from the working of a 3-ton Girod furnace which has been running since February, 1909, at the steel works of the John Cockerill Co., Seraing, Belgium, which is supplied with hot metal from a Thomas or basic Bessemer converter.

List of Girod Furnaces in Operation and Under Construction.

Cie des Forges and Aciéries Electriques Paul Girod, Ugine, France.

In Operation:

Two furnaces of 12½ tons capacity.

Three furnaces of 2 to 2½ tons capacity.

These five furnaces are generally used for treating cold charges of scrap metal; frequently, however, the 2-ton furnaces are charged with molten steel from the 12-ton furnaces. These furnaces can make four heats a day.

By tapping the two 12½-ton furnaces into a single ladle, it is possible to cast ingots of a unit weight of 25 tons, and for this purpose the steel works is provided with means for lifting, handling and casting this weight of metal.

These five electric furnaces constitute the plant of the above named company. The electric furnace steel made is afterwards worked up in the various shops of the works, which include:

One rolling mill, with two trains of rolls.

One forging shop, with one 800-ton forging press and 10-ton hammer. A 3,000-ton press is projected.

One forging shop, containing nine hammers from 175 pounds to three tons.

One steel casting foundry, with a capacity of 12 to 15 tons of steel castings per day. Castings as large as 20 to 25 tons can also be undertaken.

One fitting and finishing shop for steel castings and forgings, having 80 machine tools of various kinds.

This works, entirely operated with electric current from hydro-electric power stations, is the first electric steel works of this order erected in Europe. It does not contain a single boiler, the hammers are worked with compressed air, the rolling mills and machine tools by electric motors.

Oehler & Co., Aarau, Switzerland:

One furnace of two tons, for steel castings. Treating cold charges of scrap. Three heats per day.

Sté Anonyme, John Cockerill, Seraing, Belgium:

One furnace of three tons, for steel ingots. Charge consists of liquid metal from a basic Bessemer converter. Ten to eleven heats daily.

Stotz & Co., Stuttgart, Germany:

One furnace of two tons, for steel castings. Charged with cold scrap. Three heats daily.

All the above furnaces are in actual operation.

Among the furnaces now under construction are the following:

Ternitzer Stahlwerke, Ternitz, Austria:

One furnace holding 1,000 pounds, for fine steels. Charging cold materials.

Steirische Gusstahlwerk Danner & Co., Vienna, Austria:

One 3-ton furnace, for fine steels. Charging cold materials.

Poldihütte, Altkladno, Austria:

One furnace of 3,000 pounds capacity, for fine steels. Charging cold materials.

Marrel Frères, Rive-de-Gier, France:

One 5-ton furnace, for fine steels. Using cold charges.

Addendum: Final Additions.

(Translated by Jos. W. Richards.)

We do not use aluminium alone as a final addition to any of our steels, but we have adopted the principle of using alloys, which by their deoxidizing action give slags or mixtures of metallic

oxides more fusible than the alumina resulting from the use of aluminium alone. These new reaction materials give slags which are silicates or silico-aluminates of several metals, and in consequence more fluid.

We use particularly the following alloys:

Fe—Mn—Si—Al alloy:

Manganese	20 per cent.
Silicon	20 " "
Aluminium	12 " "

Fe—Si—Ca—Al alloy:

Silicon	45 to 50 per cent.
Calcium	20 to 30 " "
Aluminium	6 to 10 " "

Fe—Si—Al alloy:

Silicon	40 to 60 per cent.
Aluminium	20 to 30 " "

These alloys may be made in various proportions, according to the requirements of the case.

We also make and use silicon-manganese alloy of varying proportions.

When adding silicon, we prefer to add it as a rich ferro-silicon with 50 to 95 per cent. silicon, when using it simply as a deoxidizing agent; when using it, however, for introducing silicon permanently into steel, as in silicon steels, we prefer to use lower ferro-silicons carrying 25 to 30 per cent. silicon.

We also manufacture alloys composed principally of silicon, aluminium and magnesium, others of silicon, aluminium, magnesium and calcium, in any required proportions.

Our plant at Ugine, furthermore, comprises the manufacture in large quantities of various electric furnace alloys, such as ferro-silicon, ferro-chromium, ferro-tungsten, ferro-molybdenum, ferro-vanadium, ferro-titanium, ferro-tantalum, silico-manganese, titano-boron, ferro-titano-boron, ferro-vanadio-boron, etc., most of which are used or sold for use in the manufacture of special steels.

A paper read by Mr. F. A. J. FitzGerald, at the Fifteenth General Meeting of the American Electrochemical Society, at Niagara Falls, Canada, May 6, 1909; President E. G. Acheson in the Chair.

THE HÉROULT ELECTRIC STEEL FURNACE.

By Robert Turnbull,
Resident Engineer in America for Dr. P. L. T. Héroult.

As it was not certain that Dr. Héroult could arrange to be in this country at the date of the present meeting, I was asked by Messrs. FitzGerald and Bennie to present in his place a paper on the Héroult electric steel furnace.

Although much has already been published and written about the Héroult furnace, I do not think that exact data have been given showing the reasons why Dr. Héroult decided to adopt his type of furnace, and I think a little history touching on this subject would not be out of place.

Dr. Héroult's first work in the use of the electric furnace, as you are no doubt aware, was in the manufacture of aluminum. His process for the production of this metal electrically was patented in 1887, and his first furnace was of the crucible or pot type, consisting of a metallic casing the bottom of which was carbon-lined, forming one pole, whilst the movable carbon or electrode dipping into the charge to be melted and reduced formed the other one. This furnace was the basis of his work on special alloys, such as aluminum-bronze and silicon-bronze, etc. This same type of furnace, but of a different shape, was used at Boonton, N. J., in the year 1890, where Dr. Héroult made demonstrations as to the possibilities of producing various alloys which are now extensively produced in the electric furnace.

Dr. Héroult continued to use this furnace from 1890 to 1899, when the problem came up of producing low carbon ferro-chrome, and to enable him to do this he was confronted with the problem of abandoning the carbon bottom heretofore used and replacing it by some other material refractory to the alloy. His first attempt in this direction was to use a bottom lined with chromite,

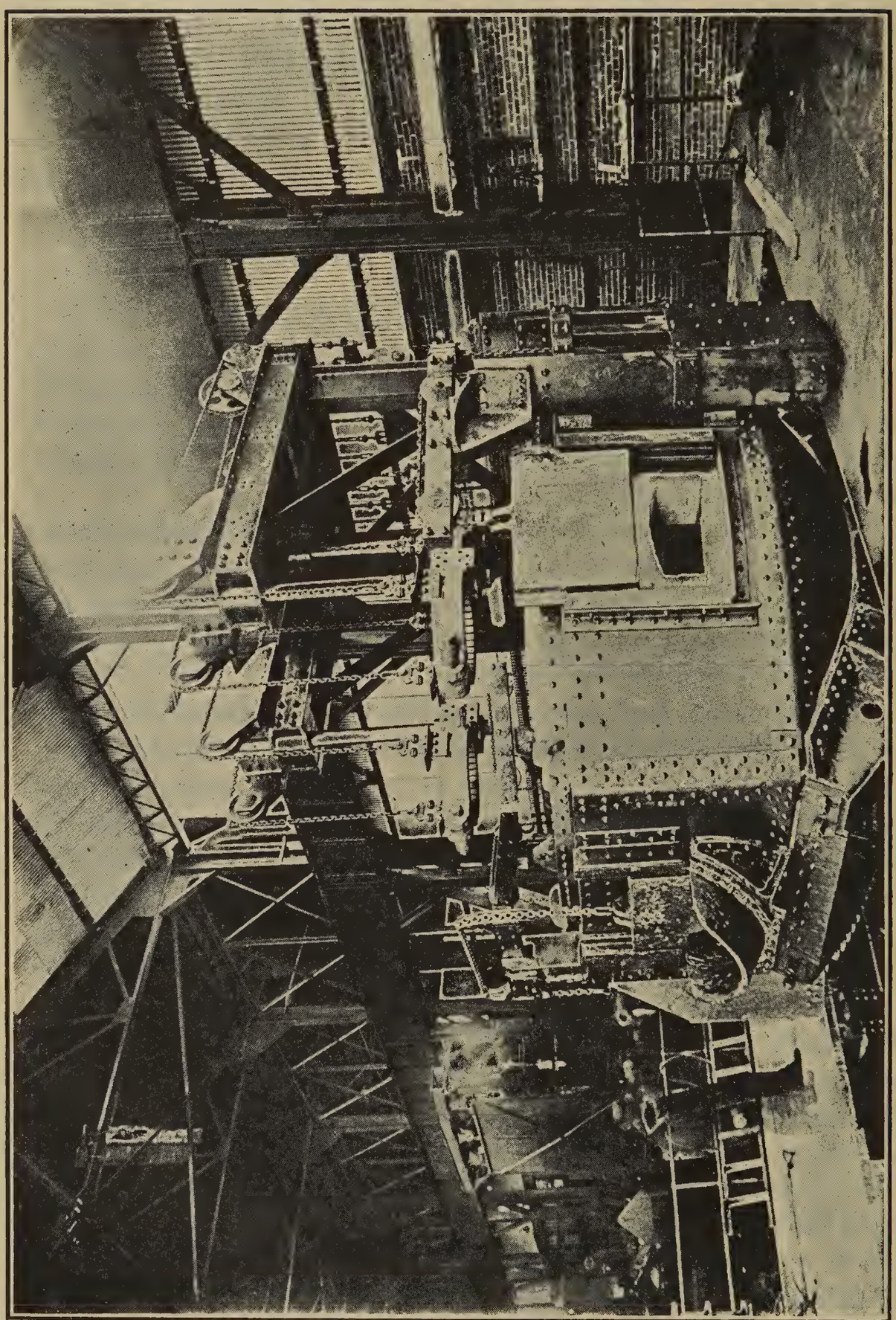


FIG. 1.—Furnace at South Chicago Works.

with a carbon rod in the center forming the lower pole of the furnace. His idea was that part of the carbon would be taken up by the metal and would be replaced by the metal itself, this process going on until the metal reached a sufficient depth, where, owing to the outside radiation, it would freeze and remain in this state, thus forming the passage for the current and preventing the contact of the carbon with the molten metal.

This scheme, although giving certain results, was soon abandoned, and after some months of experimenting the present furnace was invented. The advent of low carbon ferro-chrome brought with it the possibility of producing other soft metals, and it was not long before Dr. Héroult was at work on the steel problem, and as he already had his furnace, the production of steel became very soon an accomplished fact.

The main points which Dr. Héroult claims about his furnace are the following:

First: The total absence of electrical parts in the furnace proper, it being nothing else than a modified open hearth, with the heat introduced above the metal by the electric current in place of gas. This in itself is an important factor, as it does away with the bottom pole, always the cause of much trouble in electric furnace work, and allows of any patching necessary to the bottom or sides, without interfering with the work of the furnace.

Second: The heat being introduced by means of two electrodes working in series, the current passing through the bath from one electrode to another, and *vice versa*, necessitates carrying only half the current that would be the case should the current flow from one electrode through the bath and then through the bottom of the furnace; this cuts down all conductors to one-half the section required in the latter case and allows the electrodes to perform more efficient work, owing to the lesser density of current to be carried.

Third: The possibility of refining impure metals and transforming them into the finest grade of tool steel. The heat being generated in the slag, and not in the metal itself, makes the slag the hottest part of the furnace, and all impurities can be removed by the use of special slags. This allows the use in the Héroult furnace of the poorest kind of scrap, high in sulphur

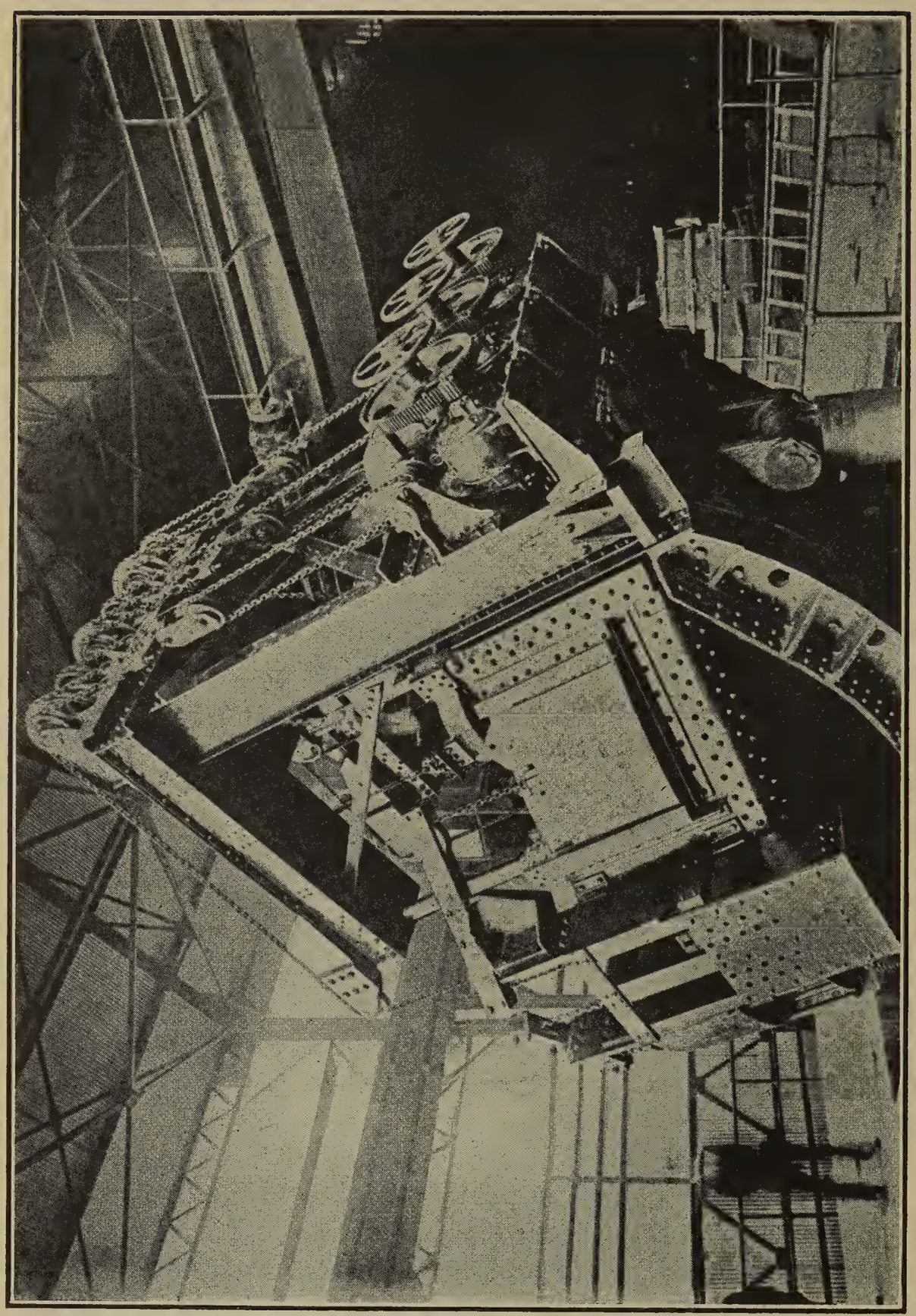


FIG. 2.—Furnace Tilted.

and phosphorus, both these impurities being removed at small cost.

I have taken as an example showing the refining abilities of the furnace the average analysis of every fifth heat out of over 80 heats, taken from a 2½-ton furnace at the works in La Praz, Savoy, France. The analysis of the scrap and product were as follows:

TABLE I.

Héroult Steel.

	Sulphur	Phosphorus	Manganese	Silicon	Carbon
Scrap Charged	0.052	0.150	0.638	0.062	0.211
Finished Steel	0.006	0.009	0.254	0.172	1.013

I am sorry that I have not received the physical tests which were made on some of the heats, but which I expect are on the way from France. I shall be glad to communicate them as soon as received to any who may be interested in having them.

The number of kw. hours necessary in the Héroult furnace to melt and partially refine one ton of steel is 600, 100 more being necessary for the finishing slag, making 700 in all. These figures are for a 5-ton furnace and starting on cold scrap; in the case of a 15-ton furnace they would be considerably reduced. Should the metal be charged hot into the furnace, that is to say, in a molten condition, and no other work be demanded outside the recarburizing, desulphurizing and deoxidation of the steel, from 140 to 180 kw. hours are necessary in the 5-ton furnace; for a 15-ton furnace this will probably be cut down to 100 kw. hours.

The life of the electrode depends on the conditions under which the furnace is run; in cold melting and continuous work the consumption is from 60 to 65 pounds per ton of steel, but in cases where the metal is charged in the molten state this consumption would only be from 10 to 15 pounds per ton, those figures including the part of the electrode which cannot be utilized.

The life of the lining depends entirely on the care with which the furnace is run; some linings will last for a year without being replaced, whilst others may have to be changed in three months.

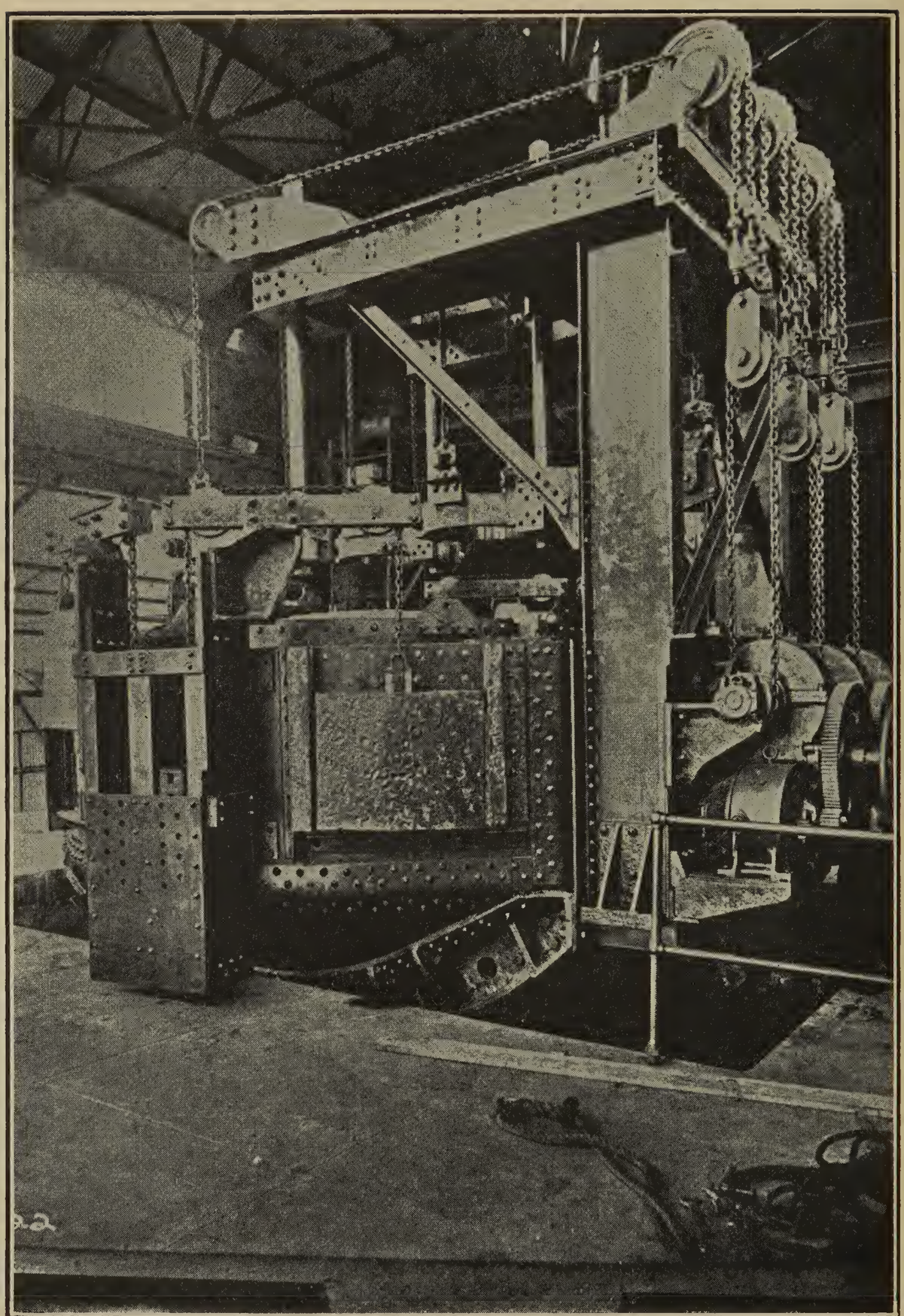


FIG. 3.—Rear View of Furnace.

In this type of furnace a lining ought to last almost indefinitely, as it is exposed at no time to silicious slags, and can be repaired after each heat by simply throwing in magnesite or dolomite as the case may be. The repairs are small; what suffers most is the roof, which has generally to be renewed once a month; as, however, a spare roof is always on hand, this can be done in a few hours.

As regards the best kind of lining for the furnace of the Héroult type, good magnesite mixed with basic slag and using tar for a binder is about the best; burnt dolomite can also be used with good results. There is no mystery about this—anyone who can make a good bottom in a basic open-hearth can do the same in a Héroult furnace.

I need not go over the list of furnaces which are at present in use or at present under construction; let it suffice for me to say that the Héroult furnace is more than holding its own in the field. I wish, however, to say a few words on our latest success in this country, and that is the adoption of the Héroult furnace in this country by the United States Steel Corporation in the manufacture of rail and structural steel, as this move on the part of the steel corporation is not only interesting to people interested in the Héroult furnace, but also to others who are working in the same field.

We are at present building two furnaces, each of 15 tons capacity, one at the south works of the Illinois Steel Co., Chicago, and the second at the works of the American Steel and Wire Co., Worcester, Mass. The furnace at the Illinois Steel Co's works is completed, and we will get the first heat out in a few days. The furnace at Worcester will not be in operation before July. The steel to be treated at the South Chicago works will be brought direct from the Bessemers, and two refining slags will be used in the electric furnace, the first an oxidizing slag to take out the phosphorus, the second a deoxidizing slag for the removal of sulphur and the gases.

The furnace is three-phase, the power being supplied by three transformers of 750 kw. capacity each, with which amount of power it is expected to turn out 16 heats a day, or about 240 tons of steel. The electrodes, of which there are three, are the largest which have so far been built in one solid block, being

FIG. 4.—An Electrode for Héroult Furnace.

two feet in diameter by ten feet long, and weighing something over 3,200 pounds. The density of current passing through these electrodes will be about 28 amperes to the square inch, a figure which we consider a little high for the work, 25 being our ordinary practice.

The accompanying photographs will give a pretty good idea of what this furnace looks like; the photographs of the furnace, unfortunately, were taken before the electrodes were put in place, but the position of the holders may be distinctly seen.

In regard to Messrs. FitzGerald and Bennie's question as to the maximum size of furnace which it is now possible to construct, it is our intention to build them up to 30 tons capacity. Very much will depend, however, on the work which has to be accomplished, that is to say, whether one or two slags would be used. In case of one slag, I have no hesitation in saying that a 30-ton furnace is possible, but should two slags be used, owing to the difficulties which might be encountered in raking off the first slag, it may be found that a 15-ton capacity is nearing the limit; it would certainly be worked quicker than one of 30-ton capacity.

In conclusion, as this is, no doubt, going to be the era of the electric furnace, I think all those interested in the production of steel should not miss the opportunity of getting in at the beginning. So far as we are concerned, I have Dr. Héroult's authority to issue a cordial invitation to any of you to visit his works at La Praz, France, where a careful study of his furnace and process can be made. We have no secrets to conceal, the work is done openly, and the operations can be conducted and controlled by the interested parties themselves, with the aid of our operators, and without any limit as to the duration of such operations.

A paper presented at the Fifteenth General Meeting of the American Electrochemical Society, at Niagara Falls, Canada, May 6, 1909; President E. G. Acheson in the Chair.

THE APPLICATION OF THE LASH PROCESS TO THE ELECTRIC FURNACE.

By Francis A. J. FitzGerald.

In a paper read at the New York Meeting of the American Electrochemical Society[1] a description was given of certain experiments made at Niagara Falls on the manufacture of steel in the electric furnace using the Lash Process. From various comments that have been made on the subject of the Lash Process there is reason to believe that the subject was not presented with sufficient clearness, and consequently various misconceptions as to what the Lash Process is and what its application might be have arisen. For this reason it seems desirable to present a more detailed analysis of the process that will bring out clearly the points of economy which the process is supposed to offer. In order to do this it is necessary to repeat things which have already been said, but as these can be expressed concisely it is convenient for the sake of clearness to allow the repetition rather than give references.

Mr. Horace W. Lash became interested several years ago in the problem of the direct production of steel from iron ore, and carried out many experiments in the investigation of this subject. The final outcome of this study was the development of the Lash Process, which might be described as a compromise between certain methods of refining and the direct production of steel from the ore. It was found that when an intimate mixture of iron ore, carbon, fluxes and cast iron borings was heated, that reduction readily took place, and that by a suitable proportioning of the mixture the desired grade of steel could be obtained.

In one of the final experiments a series of mixtures was made up in which the percentage of cast iron borings varied from a large amount to nothing, and these mixtures were then heated

[1] "Transactions of the American Electrochemical Society," **14** (1908), 239-249.

in the same furnace under exactly the same conditions. From this experiment it was learned that the mixture containing no cast iron borings did not react in a satisfactory manner, and that the presence of a certain percentage of that material was necessary in order to produce steel in a commercial way. In other words, it was found that the desired grade of steel could be produced, and that the chemical efficiency of the process or the yield of metal was very high.

From these experiments and the like the necessary data were obtained to undertake the work on a commercial scale, and since then hundreds of tons of steel have been made in the open hearth furnace using the Lash Process, and this has shown: (1) That a superior quality of steel is obtained in this way. (2) That the cost of producing the steel is in general lower than when the regular methods are employed. As regards the latter point it should be noted that the calculations on which the assertion is based are not mere estimations from certain assumptions, but are the result of the actual costs involved in a series of runs in the open hearth furnace using the Lash Process as compared with the cost of steel produced in the same plant using regular methods.

After the study of the working of the process in ordinary furnaces had been carried to a successful conclusion, FitzGerald and Bennie were engaged to make a study of the working of the process in the electric furnace, for in that apparatus certain advantages could be obtained which are not found in the open hearth furnace. In the electric furnace the atmosphere is neutral, while in the open hearth furnace it is oxidizing, thus making more difficult the proper control of the carbon content of the steel produced when the charge is melted down. In working with the open hearth furnace it is necessary to use a certain amount of pig iron or scrap, or both, in addition to the Lash mixture, while in the electric furnace this should not be necessary, and since the cost of a unit of iron in the mixture is much less than in the form of pig iron or scrap, an economy would be introduced which would offset, at least to a certain extent, the high cost of generating heat electrically. Finally, it seemed possible that the application of the process to the electric furnace, which has already demonstrated its usefulness in the manufacture

of steel under certain conditions, would, by the introduction of economies, extend the field in which it could be used.

The electric furnace experiments were carried out on a small scale at first, and it was found that the yield of metal amounted to over 98 per cent., and that the carbon content could be most accurately predicted if the original composition of the mixture was known. Following these experiments on a small scale it was planned to work in a large electric furnace of the Héroult type, and with this apparatus about 50 tons of steel were produced. The steel was of various grades, from high carbon tool steel to metal running below 0.10 per cent. in carbon. The electric furnace experiments have been described in more detail elsewhere,[2] and, therefore, we here simply mention the conclusion that steel may be produced in the electric furnace using the Lash Process with an expenditure of approximately 1.63 kilowatt hours per kilogram, or 0.25 horse-power year per metric ton.

In order to obtain a general view of the Lash Process and permit of making comparisons, a series of tables are presented. These are calculated for the production of 100 tons of steel ingots by various processes. It must be noted that the figures given for the Lash Process are based on actual practice, and are not mere assumptions. In each case it is assumed that the loss of metals amounts to approximately 5 per cent. The mixture used in the Lash Process contains cast iron borings, or granulated pig iron, ore, coke and lime. In some of the work other materials, such as sawdust and tar, have been added; the former to make the mixture porous and permit of the ready escape of the gases formed in the process of reduction; the latter to act as a binder when it was desired to briquette the mixture. For purposes of comparison, the sawdust and tar may be omitted, as they are not necessary constituents, and so far as the lime is concerned it may also be disregarded, since in any process there will not be much difference in the amount of that material used. The important constituents of the mixture then are pig iron, ore and coke. All of these must be finely divided, and since cast iron borings can only be obtained in limited quantities, it may be well to mention that there would be

[2] Ibid.

no difficulty in obtaining granulated or shotted pig iron for the mixture. Experiments were undertaken to find out if this material could be readily obtained, and as a result it was found that the pig iron manufacturers were ready to supply it at the same price as pig iron in the ordinary form.

In the tables it is assumed that pig iron contains 95 per cent. metallic iron, scrap iron 100 per cent., and ore 65 per cent.

TABLE I.

Lash Mixture.

Raw Materials	Per cent.	Per cent. Iron in Mixture
Granulated Pig iron	23	21.9
Ore	60	39.0
Coke	11	....
Lime	6	....
Total	100	60.9

TABLE II.

Production of 100 tons of steel ingots in the open-hearth furnace using pig iron and scrap.

Raw Materials.	Tons.	Tons of Iron.
Pig iron	50	47.5
Scrap	57	57.0
Ore	2	1.2
Total	109	105.7

TABLE III.

Production of 100 tons of steel ingots in the open-hearth furnace using pig iron and ore.

Raw Materials.	Tons.	Tons of Iron.
Pig iron	94	89.3
Ore	26	16.4
Total	120	105.7

In using the Lash process for the manufacture of steel in the open hearth furnace, a certain amount of pig iron or scrap must be used in addition to the Lash mixture. A typical charge for the production of 100 tons of steel ingots is as follows:

Lash mixture	122	tons.
Pig iron	32	"
Ore	2	"

On this assumption we have:

TABLE IV.

Production of 100 tons steel ingots in the open-hearth furnace using the Lash Process.

Raw Materials.	Tons.	Tons of Iron.
Pig iron	60.1	57.1
Ore	75.2	48.8
Coke	13.4	....
Total	148.7	105.9

Using the Lash Process in the electric furnace, it is not necessary to have a quantity of pig iron or scrap in addition to the mixture, so that for the production of 100 tons of steel ingots the charge would be as follows:

Lash mixture	172 tons.
Ore	2 "

Then we would have:

TABLE V.

Production of 100 tons of steel ingots in the electric furnace using the Lash Process.

Raw Materials.	Tons.	Tons of Iron.
Pig iron	40.7	38.7
Ore	103	66.9
Coke	19.5	....
Total	163.2	105.6

For the purpose of comparison the figures given above are grouped in the following table:

TABLE VI.

Comparison of different methods of producing 100 tons of steel ingots.

Raw Materials.	O. H. Furnace Scrap & Pig.	O. H. Furnace Pig & Ore.	O. H. Furnace Lash Pro.	Electric Fce. Lash Pro.
Pig iron	50 tons	94 tons	60.1 tons	40.7 tons
Scrap	57 "	. . . .	. . . . .	. . .
Ore	2 "	26 tons	75.2 tons	103 tons
Coke	. . . .	. . . .	13.4 "	19.5 "

So far as the open hearth furnace is concerned it appears evident that nothing more can be expected in the application of

the Lash Process than is shown above. It may be that some further reduction in the amount of pig iron used may be reached. The experiments with the electric furnace, however, have not been carried so far, and it is therefore probable that better results can be obtained than those which have been indicated. It may be possible, for example, to reduce the percentage of granulated pig iron used in the mixture. This possibility suggests the interesting question: Why use pig iron at all? Is it not possible in the electric furnace to use a charge consisting of ore, carbon and fluxes?

The excellent and well known work of Stassano has answered the latter question affirmatively, and he has shown that charging his furnace with a mixture of ore, carbon and fluxes, paying careful attention to the proportions, it was possible to produce steel of the desired grade. Seeking an answer to the first question, it must be remembered that Lash's experiments showed that when various mixtures containing different percentages of cast iron borings were used, it was found that the mixture which contained very little or no metallic iron failed to react in a satisfactory manner, and it was this result which in great part led to the development of the process in its present form.

If mercury and iodine are rubbed together in a mortar there is no appreciable reaction, but if the mixture is moistened with a little alcohol the mercury and iodine combine to form an iodide. The analogy is very far from being exact, nevertheless it may be used in considering the Lash experiments. Apparently the presence of the pig iron intimately associated with the mixture of ore and carbon assists in a marked way the reaction between these constituents of the charge.

Experiments have been made in the electric furnace by Mr. Robert Turnbull for the purpose of comparing the reaction of the Lash mixture and a charge containing no granulated pig iron. The results obtained confirmed the belief in the importance of the pig iron constituent, for not only was the power consumption excessive where no metallic iron was used, but the mixture boiled or frothed in a very troublesome manner instead of melting down in a relatively quiet way, which is characteristic of the Lash mixture. Moreover, where no pig iron was used the consumption of electrodes, in a furnace where the heating is

done by drawing arcs between the charge and the electrodes, is very much greater than when the Lash Process is employed.

Therefore, in answer to the question as to why pig iron should be used at all, it may be replied that its presence reduces the amount of energy required to produce a unit weight of metal from the ore, and that, by making the reaction proceed more quietly and rapidly, diminishes other expenses connected with the working of the electric steel furnace.

DISCUSSION.

MR. LOUIS SIMPSON: Might I ask the last speaker a question, Mr. President? I would like to know what he claims to be the advantage of the Lash process over the process of reducing iron ore in the reduction furnace and then afterward refining it in a refining furnace. I read his paper through very carefully, I have listened to what he has had to say, and it would seem to me that there is no advantage whatever to be gained by the process that he has described; there seems to me to be disadvantages which militate against it. I would like some light upon the subject.

MR. FITZGERALD: If I understood the question, it was: Why not produce your pig iron first, directly, in the electric furnace, then finish the refining in another furnace?

MR. SIMPSON: Yes.

MR. FITZGERALD: It is possible. One would probably have to work the two processes side by side to find out which was the more economical; but in general it means that you have to take your ore, put the whole of it through one process, then take it and put it through another process. In the Lash process a small amount of pig iron is taken, then the rest of the mixture, which is composed of ore, simply has to go through one process. That is the Lash process.

MR. SIMPSON: I fail to see the point yet, Mr. President. You have to reduce your ore in any case, and it would seem to me that it is far better to reduce your ore in a furnace specially

adapted for reduction, and then to refine the ore so reduced in a furnace specially adapted for refining.

Mr. FitzGerald: Well, that would be a matter of detail.

Mr. Simpson: I was trying to find out what reasons you had to recommend your process.

Mr. FitzGerald: The chief reason in general is that doing the thing in one process is quicker and in general more economical than doing it in two.

Mr. Simpson: I fail to see that. It is not always my experience.

Prof. J. W. Richards: Do I understand Mr. FitzGerald right, that pig iron is used, or is it cast iron in the form of cheap turnings or borings?

Mr. FitzGerald: If you can get a sufficient quantity of cast iron borings they are cheaper than pig iron. So, of course, they would be used. But if the process were worked on a large scale a sufficient quantity of cast iron borings could not be obtained; or if there was much demand for the cast iron borings the price would undoubtedly go up. Now, the criticism has been offered by more than one steel expert to the Lash process that it would be very difficult to get cast iron borings. Where are you going to get your granulated pig iron? It is a fact, if you inquire among the pig iron manufacturers, that there is no difficulty at all in getting a supply of granulated pig iron. We had quite a quantity made, the best results, I think, being obtained by pouring out the metal while the jet of steam impinged on it at right angles. Very satisfactory granulated pig iron was obtained in that way. This, then, there is no doubt about it, can be obtained just as cheaply as pig iron. In all the comparisons made in the tables, I have spoken everywhere of pig iron, because that is evidently what would have to be used.

Mr. Simpson: But my friend forgets the losses in heat. When you take your molten metal from your reducing furnace it contains a great quantity of heat, and you can take it direct to your refining furnace hot. By the Lash process you take your metal cold. Then it has to be heated up, and heat when provided electrically costs money; so it would seem to me that you are

advocating a more expensive process and one which gives no special benefits.

MR. FITZGERALD: If you are going to treat a certain amount of material, you have certainly got to heat it all up anyway. In the ordinary process, in any case, you have to start with cold ore, and that has to be heated up whichever process you use.

MR. SIMPSON: Of course, but I am considering the complete process, ore to steel. In this process you heat the iron once. In the Lash process ore has to be heated twice, once when reduced and again when made into steel.

MR. FITZGERALD: In this process you do not heat it twice.

PROF. RICHARDS: Mr. Chairman, may I remark that in the Lash process the larger part of the work is the direct reduction of ore by carbon to make steel. A minor part of the process is the putting of cast iron, or pig iron, into the charge, and the taking of that out also as steel. Now, on the one hand, you have the larger part of the steel produced from ore and carbon directly, the cheapest way of getting steel. A minor part of it is produced simply by melting pig iron; you put pig iron into the furnace and get out steel, and if that does not more than repay the cost of melting it there must be very little difference between the value of pig iron and steel. You have the entire difference between the value of the pig iron which goes in and the equivalent amount of steel which comes out to pay for the cost of the melting.

MR. H. M. LANE: I know from experience in the foundry business that the cast iron borings in an ordinary plant are a bugbear, and if some method can be found to get rid of them it will certainly pay. To-day they are used largely in the puddling process and similar processes, and we have been looking for a method of getting rid of them. For the last eight years I have been in editorial work, and I think I have written 400 or 500 letters telling men how to get rid of cast iron borings in their plants. You have to sell them for about a quarter of what you pay for them, or one-third, or whatever you can get for them. I have actually seen cast iron borings sold for $4 a ton, where the man was paying $20 a ton for his pig iron; and after it was melted up in the cupola and made into cast iron and then turned off in the machine shop, he sold it for $4 a ton because

he couldn't get any more for it. Now, with a material of that kind on the market, at a suitable price, it certainly would pay to work it in this process.

Another point, with cast iron borings there is always more or less rust. There you get iron oxide, and this process will certainly work that to advantage. If you attempt to work that in any other processes the oxide there is a disadvantage and almost bars the reactions you want to use. So I think that in this process I see an outlet for thousands of tons of iron borings at a better profit than we have yet been able to find in any other metallurgical method.

Mr. H. W. Lash, *(Communicated):* The average saving by the use of hot metal in the manufacture of open-hearth steel is about 50 cents per ton. The total cost of refining, in the basic open-hearth furnace, liquid pig iron taken direct from the blast furnace or mixer, and converting it into steel ingots, is about $3.50 per ton.

In using the Lash process, two-thirds of the steel bath is produced direct from the ore with no greater power consumption and labor cost than that required for the production of pig iron in the electric furnace. The other one-third of the bath is produced from granulated pig iron which is mixed with the ore for the purpose of acting as a solvent in presenting the free carbon in the mixture to the oxide of iron, and thereby making possible rapid and economical reduction of the latter. This would make two-thirds of the steel bath—the part produced direct from the ore—cost the same as the electric-furnace-produced pig iron, and one-third, that part produced from the granulated pig iron, cost the same as pig iron plus the cost of remelting and refining, $4.00 per ton. Therefore, the average cost of steel ingots produced by the Lash process would be, when using granulated pig iron, $2.17 per ton less than steel made from liquid pig iron, and, should cast iron borings (which are procurable in more or less quantities in every iron and steel working district, be substituted for say one-half of the pig iron in the mixture, it would lower the cost of the steel ingot to practically that of the pig iron made in the electric reduction furnace.

A paper presented at the Fifteenth General Meeting of the American Electrochemical Society, at Niagara Falls, Canada, May 6, 1909, President E. G. Acheson in the Chair.

LARGE ELECTRIC FURNACES IN THE ELECTRO-METALLURGY OF IRON AND STEEL

By Ingenieur Remo Catani.

The modern iron and steel industry has been compelled in recent years to build large furnaces in order to ensure large outputs, smallest cost price, and the most economic conditions of production. Modern blast furnaces, for instance, reach now a daily output of 400, 500 and even 800 tons; open hearth furnaces have a capacity of 20, 40 and even 60 tons; the largest electric steel furnace has a capacity of less than 10 tons.

It is doubtless true that if the electric furnace is to compete with other processes for iron and steel production, it must be of great capacity. The electrometallurgy of iron and steel is, perhaps, entirely limited by the possibility of making large electric furnaces, powerful and with large output and high efficiency.

The problem of electrically smelting iron ores and making electric steel appears to the writer as an electrical problem rather than a metallurgical one. In fact, many experiments have demonstrated not only the possibility of producing in the electric furnace all varieties of pig iron, as produced by the best managed blast furnace, smelting common iron ores; but electric furnaces have shown the possibility of smelting many iron ores which are refractory in the blast furnace, producing consequently some varieties of pig iron never produced before.

It is sufficient to remember the electrothermic experiments made at Sault Ste. Marie with roasted pyrrhotite and the production of ferro-nickel pig; the electrothermic reduction of titaniferous ore made by Mr. A. J. Rossi of New York, by Mr. Gustave Gin, by the Canadian Commission at Sault Ste. Marie, and notably the valuable experiments with ilmenite made by A. B. Greene and F. S. MacGregor in the electrochemical laboratory of the Massachusetts Institute of Technology.

In the field of electric steel, it has been shown that several electrothermic processes can produce the best qualities of high grade steel.

Increasing the power and consequently the output of a well designed electric furnace, the efficiency also, generally speaking, increases, and the economy of the installation is improved. Till now, the men engaged in the old style metallurgy have reproached electrometallurgy with producing iron and steel at too high a price. The large electric furnaces will overcome this economic difficulty that now appears to be the greatest one. In the near future, till the electric furnace will be considered as a refining rather than a direct producing furnace, electric steel will be dearer than common steel (steel rails, axles, and car-wheels, etc.), but its high price will be recognized as corresponding to its better quality, as happened before, for instance, with Bessemer steel rails *versus* iron rails, and afterwards with open hearth steel rails *versus* Bessemer steel rails.

In the following pages I will discuss some points in connection with the electrical properties of large electric furnaces using electrodes, and run by alternating current. The induction furnace has reached perhaps the largest sizes amongst the furnaces built so far for making electrically iron and steel, but my own experience has been in the line of electrode furnaces. Moreover, while the increasing of power of the electrode furnace appears as enormous in the future, it will be rather difficult to reach the same powers with the induction furnace.

I. Importance of High Efficiency.

The economic question for a metallurgical process, whether it shall employ coal or electricity, is not only dependent upon the prices of coal and power, which change from one country to another, but depends also upon other considerations, above all upon the efficiency of the electric furnace, which has the same value everywhere. For instance, if we could reach practically the figure given by Dr. Héroult, 120 tons of pig iron per day from a power plant of 10,000 horse-power, the electrothermic reduction of iron ores should be possible even when the cost of a horse-power-year is rather high.

In a paper read before the "Associazione Elettrotecnica Italiana" at its last meeting, held in Rome October, 1908, I stated that blast furnace pig iron and electric pig iron have the same cost price when:

$$x = \frac{1}{0{,}115 + \frac{4}{n}}\, y$$

where:

x is the cost of a horse-power-year, in lire.

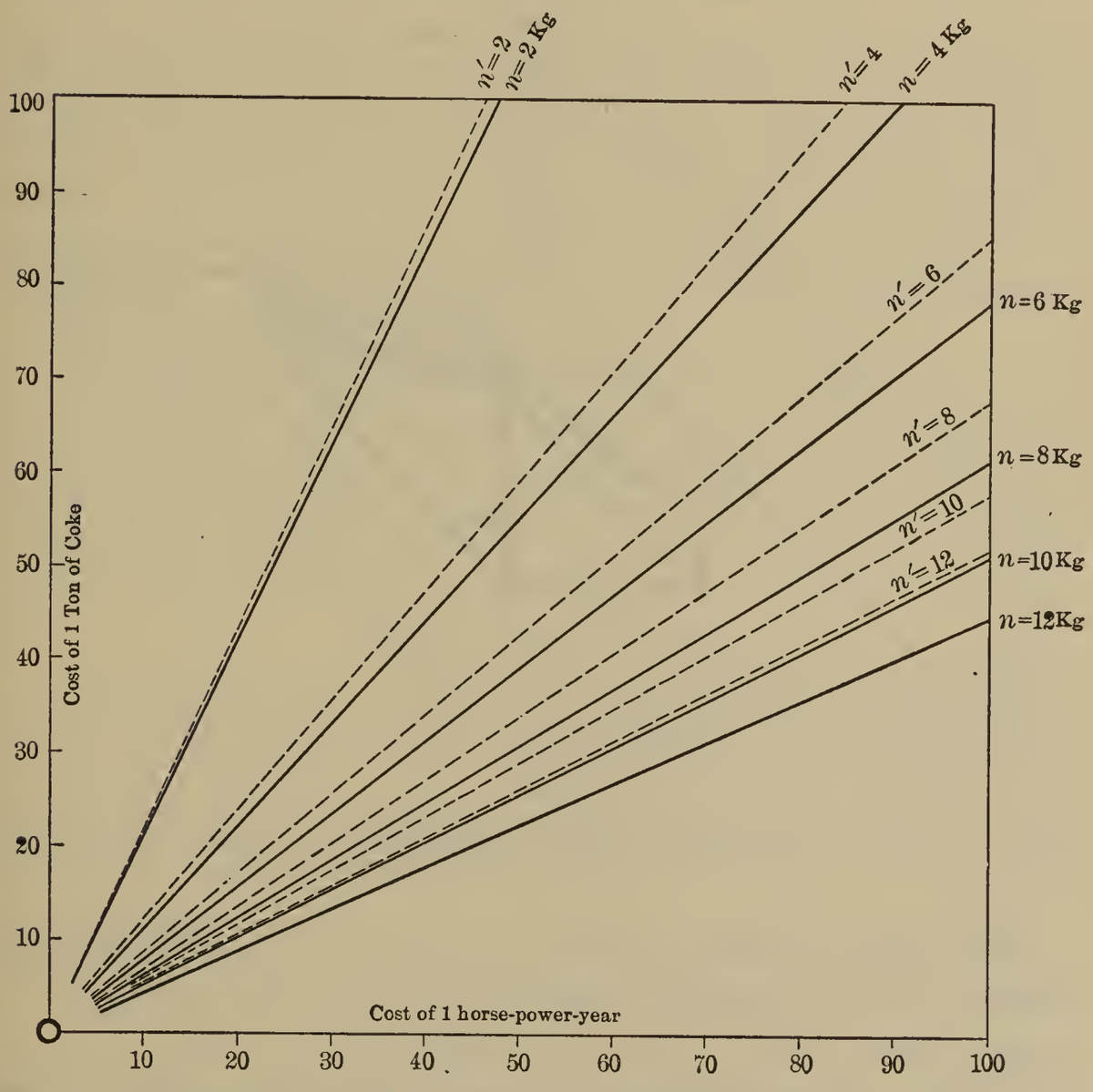


FIG. 1.—Comparative Economy of Electric Furnaces and Blast Furnace Iron, Using the Gases of Both Furnaces.

y is the cost of a ton of coke, in lire.

n is the number of kg. of pig iron produced per horse-power-day.

In the above formula, the writer assumed that the gases of

both blast and electric furnaces are entirely utilized in gas engines, and a year is composed of 8,000 hours.

In Figs. 1 and 2 is shown the comparative economy of electric and blast furnace running. In Fig. 1 every point of the lines corresponds to a relation between x and y, for which the cost price in the two processes are equal; for all the points above each line electric reduction is more economic than that in the blast furnace.

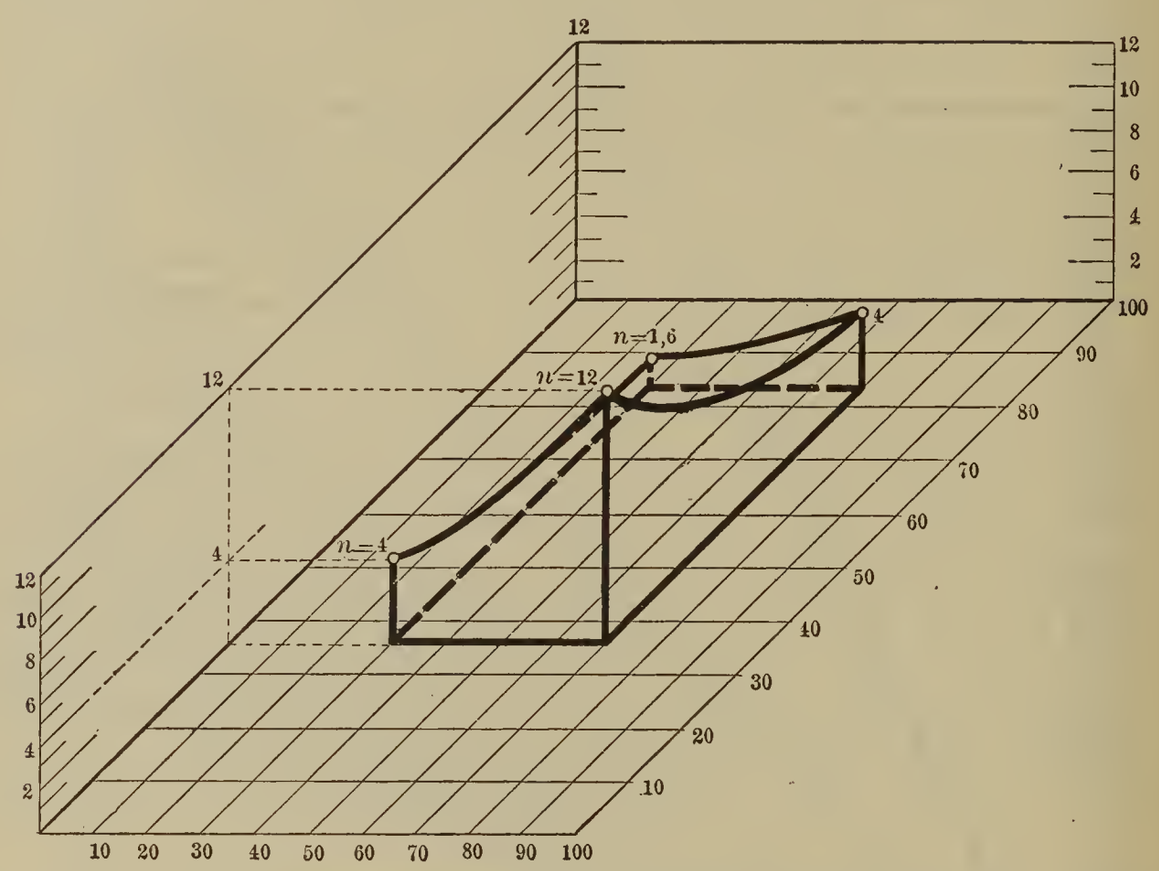


FIG. 2.—Comparative Economy of Electric and Blast Furnace Iron, Not Utilizing the Electric Furnace Gas.

The diagram shows also that a wide field of economical application of electric furnace is included between the lines:

$n = 12$ $n = 4$

In Fig. 2 the discussion is limited within the values corresponding to the countries rather poor in coal and sufficiently rich in power (as water power, coke or blast furnace gas power, etc.).

For a given value of x or y, as the diagram shows, n varies hyperbolically with y or x. This fact proves the importance of furnace efficiency in the economic study of electric pig iron.

II. Utilization of Electric Furnace Gas.

In my further researches, of which the present paper is the first publication, I have found that if only blast furnace gas is utilized, the preceding formula would be changed as follows:

$$x = \frac{1}{0{,}185 + \frac{4}{n}}\, y$$

from which we have, for $n = 12$, very approximately

$$x = 2y$$

or, in other terms, electric pig iron should cost as much as blast furnace pig iron when the price of a horse-power-year is twice the price of a ton of coke, and the electrothermic reduction of iron ores should be cheaper than that in a blast furnace, when a horse-power-year costs less than two tons of coke.

In Fig. 1 are drawn also the straight lines representing the variations of n with x and y.

The diagram shows that the utility of the employment of the electric furnace gas increases with the efficiency of the furnace. While with a production of 2 kg. of iron per horse-power-day the utilization of the gas is almost useless; for 12 kg. the utilization appears as necessary.

III. Power Factor.

The power factor is very different according to the different types of electrical furnaces; in the report of the Canadian commission of 1904 it is found a minimum cos. $\varphi = 0.375$, corresponding to 64.5 volts, 6,185 amperes, 37 cycles. In the report on the experiments made at Sault Ste. Marie was found a maximum cos. $\varphi = 0.94$ for 39.2 volts, 5,040 amperes, frequency 30 cycles.

The power factor must be as high as possible, and it is possible to increase it by lowering both the frequency and the co-efficient of self-induction.

Notwithstanding, if an electric furnace gives a satisfactory power factor, that is not constant for all the charges of the furnace. In fact, it is known that:

$$\sin.\ \varphi = \omega\ L\ \frac{I}{E} = 2\ \pi\ L\ \frac{I}{E}$$

where

ω = frequency.
L = coefficient of self-induction.
I = current in amperes of the furnace.
E = voltage on the furnace.

For a given furnace ω, L and E are constants; sin. φ, and also φ, is increasing with I; cos. φ is diminishing. In order to have a constant power factor, at every value of I, it should correspond to such a value of E that the ratio $\frac{I}{E}$ should be constant.

The above formula is suitable to calculate φ, for any other value of $\frac{I}{E}$, when φ is known corresponding to a value of $\frac{I}{E}$.

For instance, if we take into account the electrical tests made at Sault Ste. Marie and reported on page 5 of the report, from the first experiment we have:

$$\cos.\ \varphi = 0.922; \qquad \sin.\ \varphi = 0.387$$
$$E = 39.8 \qquad I = 5447$$

The formula gives:

$$0{,}387 = \omega L \frac{5447}{39.8} = K \frac{5447}{39.8}$$

from which

$$K = \omega L = \frac{2{,}82}{10^3}$$

For other values of $\frac{I}{E}$ we have:

$$\sin.\ \varphi = \frac{2{,}82}{10^3} \left(\frac{I}{E}\right)$$

With this formula has been calculated the following table:

E	I	Cos. φ from True and Apparent Watts	Cos. φ from the Formula
39.8	5447	0.922	0.922
40.0	5337	0.923	0.926
40.1	5377	0.928	0.925
39.2	5040	0.940	0.932
38.7	5096	0.937	0.928

The frequency was constant and of 30 cycles. The difference between 5447 and 5040, maximum and minimum values of I,

is only 7 per cent.; the power factor increasing from 0.922 to 0.940, about 2 per cent.

For larger increase of the current, the dropping of the power factor is very considerable, as it appears from the diagram shown in Fig. 3. The diagram reviews my experiments on a monophase furnace, with a single arc, 42 volts, 25 cycles.

Voltage being constant, the current was raised from 7,500 amperes to 14,000; the power factor dropped from 0.912 in the former experiment to 0.65 in the last one.

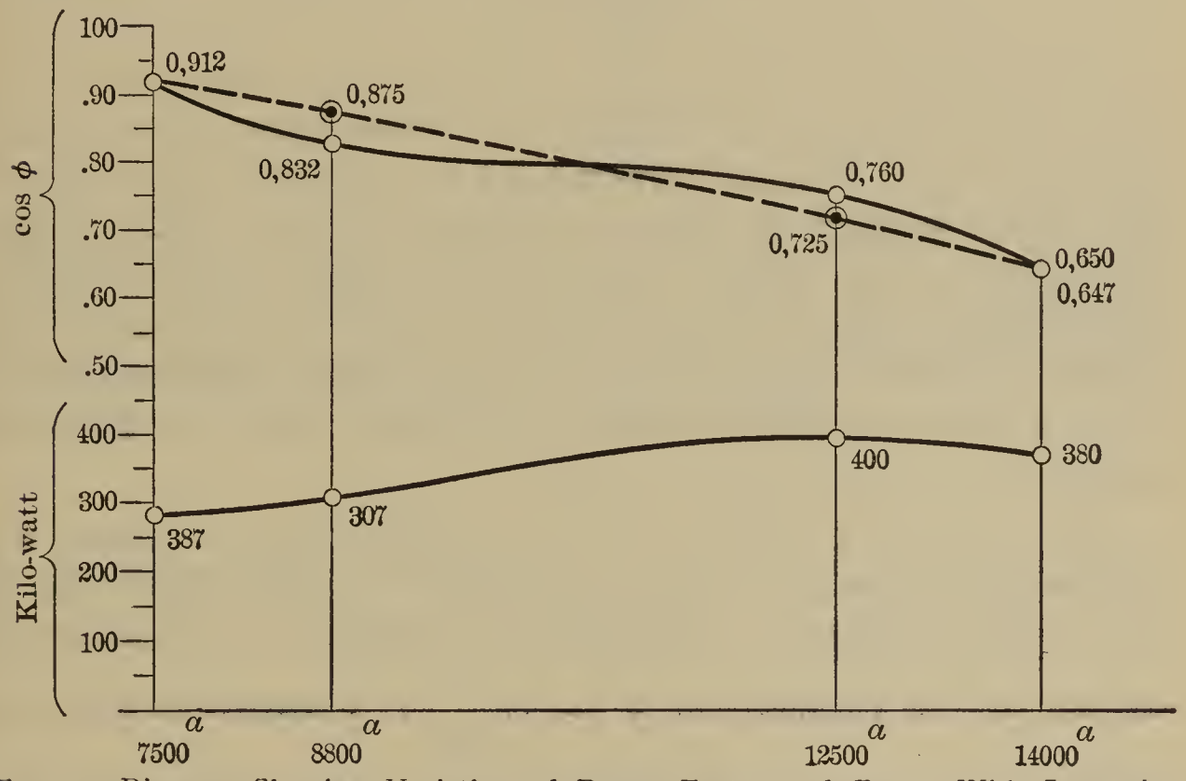


Fig. 3.—Diagram Showing Variation of Power Factor and Power With Increasing Current.

A furnace of a new type presented a loop formed by the current circuit of a very small area.

Proceeding as before we have:

$$\cos.\ \varphi = 0{,}912; \qquad \varphi = 24^\circ 13'; \qquad \sin.\ \varphi = 0{,}410$$

$$0{,}410 = \omega\ L\ \frac{7500}{42}$$

$$\omega\ L = \frac{2.3}{10^3};$$

and remembering that

$$E = \text{constant} = 42 \text{ volts}$$

the relation between φ and I is:

$$\sin.\ \varphi = \frac{55}{10^6}\ I$$

from which are calculated the figures of the last column of the following table.

E	I	Cos. φ	
		From Kilowatt-meter	From the Formula
42	7500	0.912	0.912
	8800	0.832	0.875
	12500	0.760	0.726
	14000	0.650	0.647

In the diagram are drawn the curves corresponding to cos. φ from kilowatt-meter and formula; also the power curve. The power increased with the current till I = 12,500; between 12,500 and 14,000 amperes the current increased 12 per cent., but the diminution of the power factor was so great that the power decreased from 400 to 380 kw. with a drop of 5 per cent. The furnace was for 10,000 amperes, the upper electrode being composed of four amorphous carbons, 250 mm. x 250 mm. grouped together.

Fig. 3 shows that the calculated curve of cos. φ is not too different from the true values observed, even when the rising of the current is great. Consequently, designing a furnace with the aid of the formula $\sin \varphi = L \frac{I}{E}$, it is possible to draw the curves of cos. φ and of the power for any value of the ratio $\frac{I}{E}$.

When a variable charge in the furnace is expected—as is the general case—it is advisable to design the means to change simultaneously I and E in such a way that the ratio $\frac{I}{E}$ is nearly constant. Otherwise the increasing in power will be only apparent, or, at least, not so great as it appears from the readings of I and E, and assuming a constant power factor.

It is probable that the future large furnaces will be increased in power by raising both voltage and current. This is, perhaps, rather different from what has been written by several authors who think that the power of an electric furnace is dependent only upon current.

IV. Self-induction.

From the first and second case discussed we now have:

$$L = 2\,\pi\,n\,L = \frac{2.82}{10^3}$$

$$\omega\,L = 2\,\pi\,n\,L = \frac{2.3}{10^3}$$

from which, remembering that the frequency was, respectively, 30 and 25 cycles

$$L = \frac{14.97}{10^6}$$

$$L = \frac{14.65}{10^6}$$

The slight difference between these values is to be noted, although the furnaces were quite different from each other, except that both were small furnaces. For more powerful furnaces L ought to be lowered—the more the larger the furnace.

In fact, let us consider again the relation:

$$\sin\varphi = 2\,\pi\,n\,L\,\frac{I}{E}$$

It may be written as follows:

$$2\,\pi\,n\,L\,\frac{I}{E} < 1$$

$$I < \frac{E}{2\,\pi\,n\,L}$$

But the voltage E cannot reach such a high value as to produce a difficult run of the furnace; I must be raised if it is wished to increase the power; then L must be lowered.

An illustration will explain better these facts. Fig. 3 shows that, in the furnace I tested, the maximum power was obtained when cos. φ was about 0.75.

Therefore sin ϕ = 0.66

$$0.66 = \frac{2.3}{10^3}\,\frac{I}{E}$$

$$I = \frac{660}{2.3}\,E = 287\,E$$

$$W = E\,I\,\cos.\,\varphi = 0.75 \times 287 \times E^2$$

If the power is expressed in kw. and the voltage in volts, we have:

$$W = 0.215\,E^2$$

The practical maximum voltage may be assumed as 100 volts, and then we have:

$$W_{max} = 2150 \text{ kw.} = 3720 \text{ horse-power}$$

A more powerful electric furnace should be designed in another way, lowering the frequency or the coefficient of self-induction or both.

Of course, to lower L is a more interesting problem than that of lowering the frequency, because very often it is a question of making a larger electric furnace using a given current; but even when the installation is being designed, it is not convenient for the electrical machinery to lower very much the frequency. I consider the 25 cycles as the best frequency for electrometallurgical purposes.

For a new furnace the coefficient L may be either approximately calculated with some one of the formulas given, or measured with some one of the practical methods suggested by electrometallurgists. Nevertheless, improvements are always necessary after a testing run of the furnace.

V. Monophase Furnace Versus Triphase Furnace.

It is sometimes said that in a triphase furnace cos. φ and the efficiency have a very high value because self-induction is the minimum.

Instead, as it has been shown in a preceding paragraph, it is possible to have a high cos. φ even with a monophase furnace. Moreover, in a triphase furnace cos. φ decreases very quickly, dropping the current. It is probable that with one-quarter load—as it happens with the poliphase motors—cos. φ is very low, above all if the load is not uniform.

Also, it has been thought recently that it is easier to make big furnaces using triphase rather than monophase current. Perhaps this opinion is born because the most powerful furnace in the world, as far as I know, is a triphase one. This furnace has been built in Sweden for making calcium carbide and ferro silicon. Its power is about 7,000 horse-power; each pole is composed of ten electrodes of which the dimensions are approximately 30 x 30 x 150 centimeters; the electric characteristics

are I = 45,000 amperes, V = 80 to 100; the crucible is not traversed by the current; the furnace has three tapping holes.

Under the same conditions of voltage, current, cross section of electrodes, and power factor, a monophase furnace is more powerful than a triphase one.

In fact, given as before:

E, I, cos. φ = the voltage, current and power factor of the circuit,

d, a given number of amperes per unit surface,

S, a given total cross section of the electrodes put in the furnace.

Then:

$$I = S.d.$$

The powers, W, of the different types of electric furnaces are as follows:

I. *Monophase Furnace.*

a With a single arc

$W_1 = d.S.E.\cos.\varphi.$

b With two arcs in series

$$W_2 = 2\ d.\ \frac{S}{2}.\ E\ \cos.\ \varphi = d.\ S.E.\ \cos.\ \varphi.$$

II. *Triphase Furnace.*

$$W_3 = \sqrt{3}\ d.\ \frac{S}{3}.\ E.\ \cos.\ \varphi = 0.577\ d.\ S.E,\ \cos.\ \varphi.$$

From this formula:

$$W_2 = W_1 \qquad W_3 = 0.577\ W_1$$

$$W_1 = 1.73\ W_3$$

The Swedish triphase furnace described before, if changed to a monophase one, would have a power, without any change in its dimensions, of about 12,000 horse-power, instead of 7,000.

A triphase furnace versus a monophase furnace of the same power presents some peculiar features of which a few are considered as advantages and others as inconveniences.

The former may be summed up as follows: Neutrality of the hearth; greater facility of making the furnace rotary, above all if electrodes remain in their lines during the rotation; cheaper electrical machinery (alternators, line, transformers, etc.). As inconveniences may be considered the following features:

Larger cross section of electrodes put in the furnace; greater number of electrode holders or larger electrode holders in an unfavorable position, being exposed to the radiation of the furnace; necessity of running to full load or over load in order to have a good efficiency; possibility of short circuit through the walls of the furnace without passing of the current through the bath (it is to be remembered that the voltage between electrodes s $\sqrt{3}E = 1.732\ E$, whilst between electrodes and bath is E); larger dimensions of the furnace.

Of course, some of these inconveniences can be overcome. A few can be eliminated, but by introducing other ones; for instance, the inconvenience of the short circuit through the walls of the furnace is eliminated by enlarging the linear dimensions of the furnace, but, then, the last of the above named inconveniences appears.

VI. Maximum Powers in Electric Furnaces.

It has been seen that if the Swedish triphase furnace discussed in V could be fed with a monophase current at the same voltage, its power will increase from 7,000 to about 12,000 (and perhaps more) horse-power. Assuming a practical maximum voltage of 100 volts, a frequency of 25 cycles, and a power factor of 0.75, we have

$$\text{sin. } \varphi = 0.66$$

$$0.66 = \frac{2\ \pi\ n}{E} L\ I = \frac{\pi}{2} L\ I$$

$$L\ I = 0.42$$

If a furnace of 10,000 kw. $= 10^7$ watts is to be designed, we must have:

$$10^7 = I\ E \cos.\ \varphi = 0.75 \times 100 \times \frac{0.42}{L}$$

Therefore:

$$L = \frac{3.15}{10^6}$$

Then the coefficient of self-induction ought to be about one-fifth of that corresponding to the two types of furnaces discussed in III.

In studying the means of reducing L it is to be remembered

that it depends upon the permeability μ of the field, and then it is necessary to avoid in the furnace construction any material of high permeability, at least in the loop formed by the conductors of the current.

From these considerations is derived the possibility of making very powerful electric furnaces, much more powerful than those built up to now, corresponding to the very large electrical powers actually reached in steam or water turbines, alternators, transformers, etc., and we may hope that if such powerful electric furnaces will be built, electric furnaces will produce iron and steel at as low a price as the best common metallurgical furnaces.

Portoferraio, Italy,
March, 1909.

DISCUSSION.

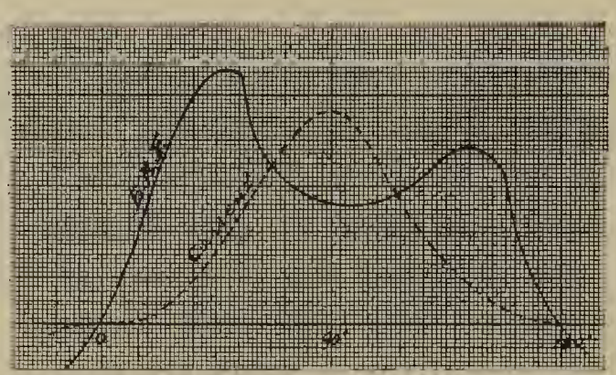
Prof. J. W. Richards: I wish to say that I had the pleasure of meeting Mr. Catani on the Island of Elba last January and found him experimenting with some 1,000 kw. furnaces at the works of the Societé Elba, for which he is consulting engineer. They were trying two or three different kinds of electric plants to utilize the power generated by gas engines from their blast furnaces. They are reducing the iron ores of Elba right on the spot, generating power from the blast furnace and coke oven gases with gas engines, have a large surplus of power, and are considering entering the calcium carbide industry and the production of steel. Mr. Catani's paper is particularly directed toward this latter point.

Mr. Carl Hering (*In the Chair*): There are advocates here of the three-phase furnace, and now Mr. Catani shows us that it will be much better to make monophase furnaces out of them. It seems to me this would be a point well worth discussing. We are all anxious to know which is the better. I doubt whether Mr. Catani has considered the question of the transmission of the energy for a monophase furnace as distinguished from a polyphase furnace. Power from a distance is usually transmitted as a polyphase current, and it would therefore have to be changed to a single-phase current before it could be used in that form.

and that requires expensive machinery. The question, therefore, naturally arises: Is the alleged gain in monophase furnaces worth the additional cost of the power and the extra machinery? When current is generated on the premises, this does not apply.

Mr. Joh. Härden: Mr. Catani speaks of the power factor and the possible means of increasing the same. These are based upon the assumption that the power factor observed on various arc furnaces follows a sine-function. This, however, is only the case in induction furnaces, either simple or combined (Röchling-Rodenhauser system). But the power factor in an arc furnace is, as far as experience has taught, not only a function of the self-induction caused by the magnetic field, set up by the cables and electrodes, etc., but we have also to deal with what is termed the "impurity factor."

This is characterized by the fact that the e.m.f. and the current are in phase when passing in the neighborhood of or through zero, but will be out of phase between the zero points as shown in the accompanying curve.



This will on the volt-ampere and watt meters manifest itself as a power factor, but it is by no means a sine-function, and has very little to do with the self-induction. Hence, the arrangements of the cables, etc., will have little or no influence upon this feature. The frequency will have an opposite effect, if any, *i. e.*, a lower frequency will cause a greater lag between e.m.f. and current between the zero points than a higher.

It must be admitted, however, that if the space between the electrodes is sufficiently heated so as to conduct the current without any considerable increase of the initial e.m.f. for each half period, the effect will be less prominent, but ought to be considered in the design of a large furnace with low voltage and very heavy current.

A paper presented at the Fifteenth General Meeting of the American Electrochemical Society, at Niagara Falls, Canada, May 6, 1909, President E. G. Acheson in the Chair.

THE KJELLIN AND RÖCHLING-RODENHAUSER ELECTRIC FURNACES.

By Dr. F. A. Kjellin.

I. The Kjellin Electric Induction Furnace.

History.

Early in the year 1899 I was approached by Mr. Gustaf Benedicks, general manager of the old iron works at Gysinge, Sweden, who asked me if I could build him an electric furnace at Gysinge for the production of the highest class of tool steel from the Dannemora iron produced at Gysinge.

After studying almost all types of electric furnaces which were then described in the technical literature, I came to the conclusion that none of them would suit the purpose. My main objection to them all was the difficulties caused by the electrodes, and I started considering the possibility of overcoming those inconveniences. At last I found what I then considered a quite new way of dispensing with the electrode difficulties altogether. This could be done by constructing the furnace in such a way that the molten steel formed an annular ring, and by using this ring as the secondary of a step-down transformer. I put my ideas before Mr. Benedicks, who agreed to my project; and in May, 1899, I went to Gysinge to build an experimental furnace.

In February, 1900, this furnace was ready for use, and by March 18th the first steel ingot was cast.

When I had convinced myself concerning the practical possibility of my ideas, I applied for a patent covering the whole field of induction furnaces; but the patent authorities soon proved to me that I was not the first one in this field, as in 1887 similar patents had been applied for by Mr. Colby in the United

States, and Mr. Ferranti in England. Consequently I had to restrict my claims to cover the special arrangements I had used for carrying out my ideas.

In the meantime the small furnace at Gysinge was gradually improved until it produced, with 58 effective kilowatts, 600 to 700 kg. of steel ingots in 24 hours. The charges were about 100 kg. each, and the time between the teemings from three to four hours.

The results were encouraging, although not commercially satisfactory, because of the small scale, and when in the end of 1901 more water power was available at Gysinge, we did not hesitate to build a larger furnace. This furnace was ready to start in May, 1902, and proved an entire success, so that from that time steel melting in induction furnaces may be said to have reached a commercial scale as far as the production of high quality steel is concerned.

The output of this furnace was about four tons in 24 hours with 225 electric horse-power, and each tapping was about one ton. One of the new features of this furnace was the use of a magnesite lining instead of the silica bricks used in the small furnace. The result from this change of lining was that we got rid of the high percentage of silicon which formerly was taken up from the lining, and that the life of the lining was considerably increased. With the acid lining we had to re-line about once a week, but the first time that the lining was tamped in with magnesite it lasted twelve weeks, which was a record that we have not beaten since. This furnace has been working continually since that time for the production of high quality steel. It was for a long time the only one of its kind, and it was only when the task of introducing the furnace on the European continent had in 1904 been placed in the hands of the well known electrochemist, Dr. Victor Engelhardt, that its rapid development began. It is chiefly due to his work that the induction furnace has now been adopted by some of the most prominent makers of high class steel in Europe. Among the first who took a license for the use of the Kjellin furnace was the Röchling'sche Eisen und Stahlwerke, Völklingen, whose general manager, Mr. Hermann Röchling, had personally studied the furnace at Gysinge. Their idea was to use the furnace for

refining basic Bessemer steel from their converters, but they soon found that the furnace in its original form was not adapted for working with dephosphorizing and desulphurizing slags. The form of the bath, an annular ring, was not very convenient, and offered too small a surface to the attack of the slag. They therefore worked out a modified furnace, generally known as the

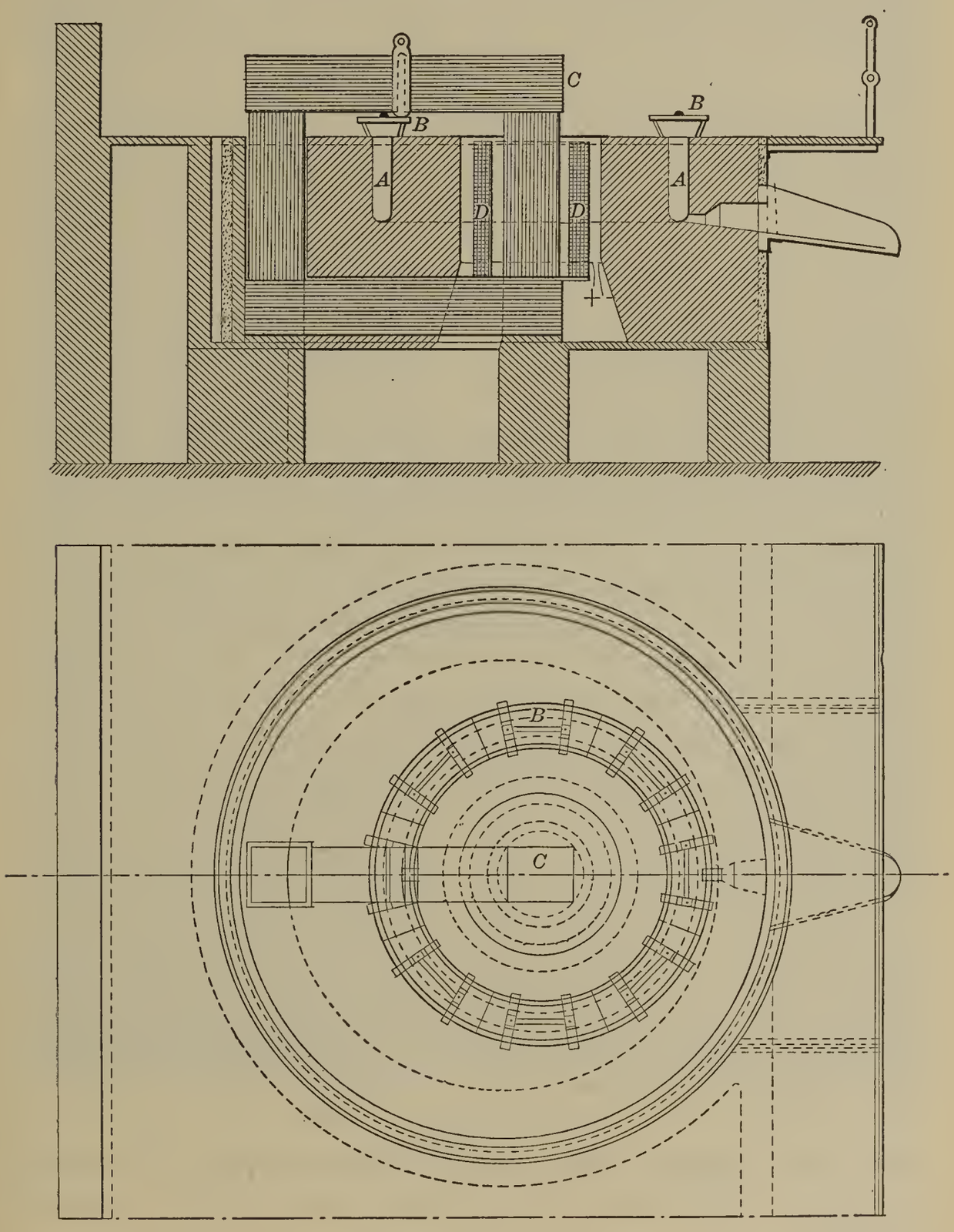


FIG. 1.

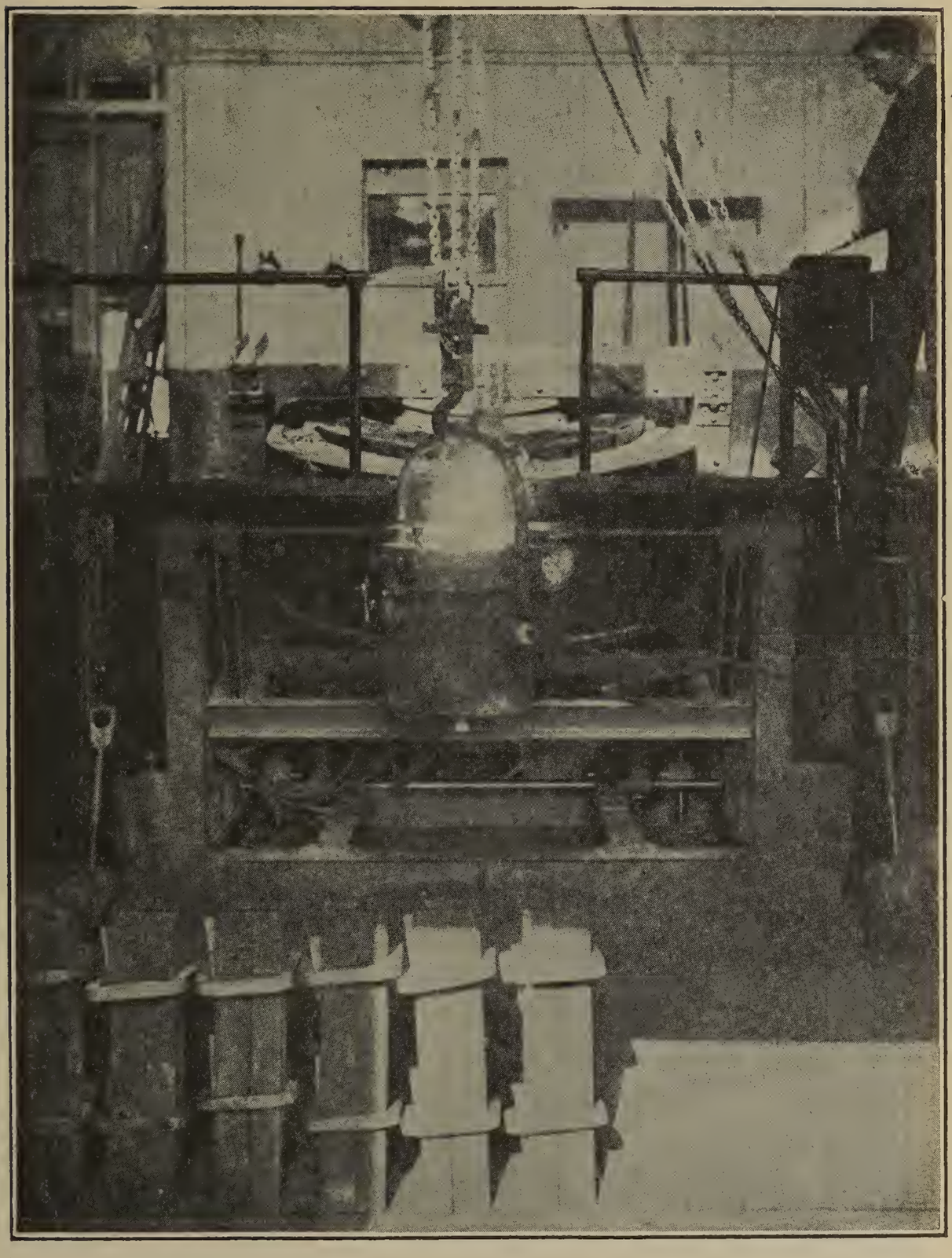
"Röchling-Rodenhauser" furnace, Mr. Rodenhauser being the inventor of that modified furnace.

In this furnace they have combined two annular rings so that they form something like the figure 8, and the main central bath is common to both the circuits formed by the rings. This bath is then heated by the currents induced in both circuits, and also by the current from extra secondary coils passing through the electrically conducting lining of the furnace to the molten steel.

The illustration (Fig. 1) shows the principle of the Kjellin furnace. It is in reality a transformer, in which the bath of molten metal forms the secondary circuit. The magnetic circuit C is built up of laminated sheet iron like the core of a transformer. The primary circuit is a coil D, consisting of a number of turns of insulated copper wire or tubing surrounding the magnetic circuit. The ring shaped crucible A, made of suitable refractory materials, also surrounds the magnetic circuit, and when filled with molten metal forms the secondary circuit of the transformer. The annular crucible is supplied with covers B.

When the coil D is connected with the poles of an alternating current generator, the current, when passing through the coil, excites a varying magnetic flux in the iron core and the variation in the magnetic flux induces a current in the closed circuit formed by the molten metal in the crucible A. The ratio between the primary and secondary current is fixed by the number of turns of the primary, and the magnitude of the current in the steel is then almost the same as the primary current multiplied by the turns of the primary coil. Thus, in a small furnace of this type a current of 500 volts and 280 amperes supplied to D induces a current of seven volts and 20,000 amperes in the metallic bath.

The method of working the induction furnace is peculiar to itself, because it is not possible to fill the crucible with broken pieces of pig iron or scrap and melt this down, the voltage of the induced current being far too low for this. Instead, an iron ring must be placed in the crucible and melted down to form a bath, or the crucible must be filled with molten metal taken from another source. In continuous working the custom is to leave a sufficient amount of metal in the crucible to establish the bath.



ILLUS. 1:
Tapping 1,000 Pounds of Tool Steel From a Kjellin Induction Furnace.

Production of high class steel from cold scrap and cold pig iron: Raw materials—white Dannemora pig iron from Gysinge ore; Walloon bar ends.

AVERAGE ANALYSIS.

	Pig iron.	Bar ends.
Carbon	4.40%	0.20
Silicon	0.08%	0.03
Sulphur	0.015%	0.003
Phosphorus	0.018%	0.009
Manganese	1.00%	0.12
Copper	0.015%	0.008
Arsenic	0.035%	0.0035

ANALYSIS OF PRODUCT AND TENSILE TEST.,

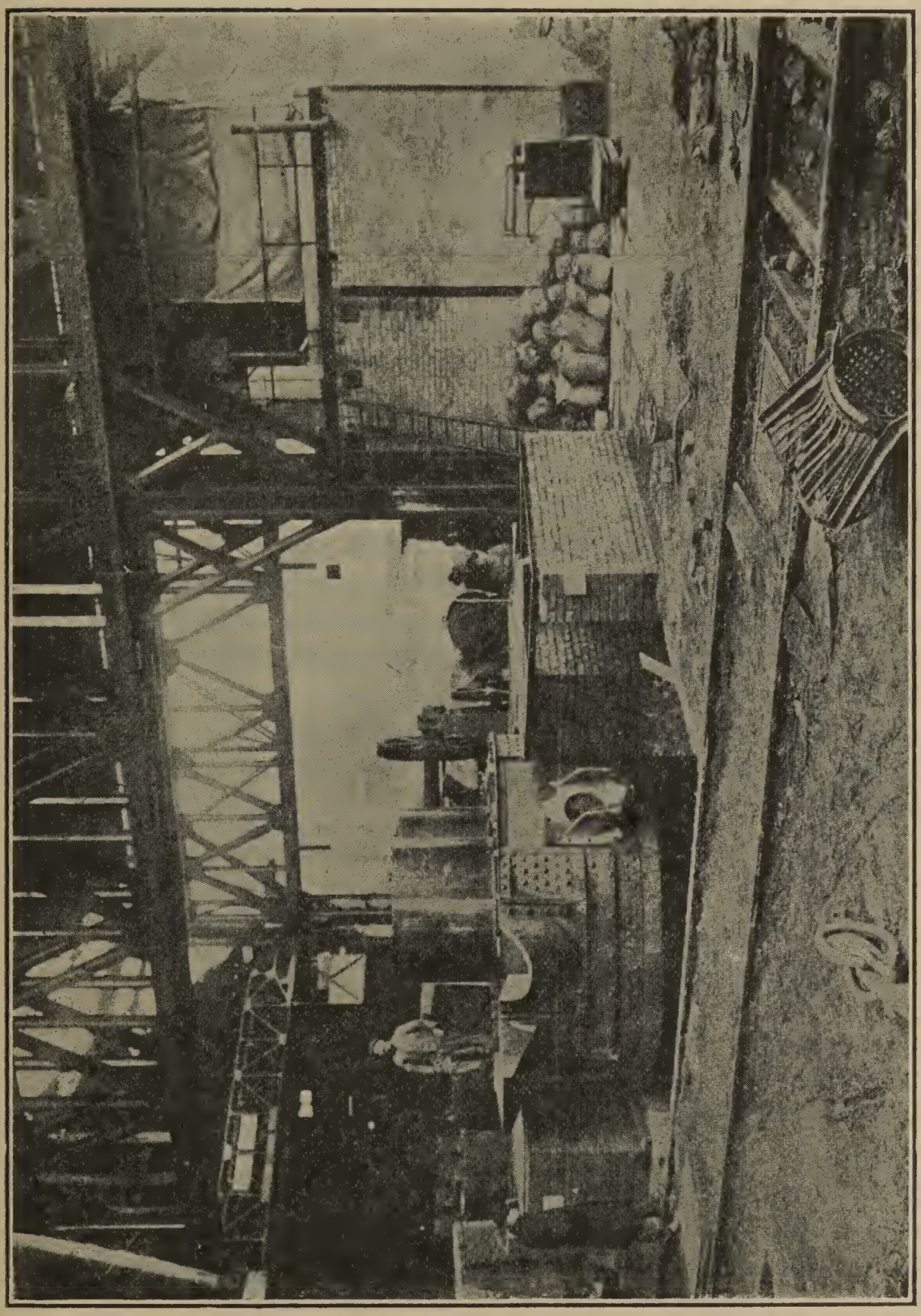
Test pieces annealed. Diameter, 20 millimeters. Elongation measured on 200 millimeters.

Proportionality limit %	Yield point *	Tensile Strength *	Elongation %	C. %	P. %	Si. %	Mn. %	S. %
38.2	80,500	109,600	0.5	2.32	0.015	0.21	0.77	0.011
44.0	72,400	136,700	7.1	0.91	0.019	0.23	0.33	0.011
44.3	71,900	138,500	10.6	0.91	0.018	0.30	0.47	0.010
33.0	61,400	105,100	10.0	0.89	0.015	0.27	0.30	0.005
33.8	68,500	134,700	9.0	0.80	0.015	0.27	0.48	0.007
36.1	57,900	107,900	15.0	0.63	0.017	0.30	0.44	0.008
30.2	47,400	61,400	23.8	0.18	0.014	0.12	0.17	0.008
14.3	28,200	45,500	28.0	0.07	0.013	0.012	0.06	0.009

As to peculiar qualities of the steel caused by the treatment in an induction furnace, my experience tends to support such an idea, and I can cite two striking examples:

When some years ago I visited one of the most prominent crucible steel works in France, I showed to the manager, as a curiosity, a bar of steel about one inch square with over 2 per cent. of carbon, which had been twisted cold so that it looked like a corkscrew. The manager told me that he thought the same result could be obtained with their crucible steel, and offered to prove it. For this purpose he made from Gysinge pig and bars, which they had in stock, a steel with the same carbon as mine, had it forged out and annealed and twisted cold. The result was that the steel broke long before it had been twisted as much as mine. Another time I had the pleasure of seeing at Gysinge one of the best quality steel makers of the European continent, who came there with his own raw materials in order to melt them in the induction furnace and compare the product with the product he got at home with the same

* Pounds per square inch.



ILLUS. 2:
8.5 ton Kjellin Furnace at Völklingen.

materials in crucibles. The result was that he could make his steel in the induction furnace with less additions of silicon and manganese than was necessary in the crucible. Trials made at Völklingen with a Kjellin furnace have also proved that molten Thomas-Bessemer steel poured in a Kjellin furnace and simply left there for some time has improved remarkably in quality.

The only probable explanation I can think of is that the higher heat in the induction furnace expels a portion of the gases dissolved in the steel and perhaps also facilitates the removal of the combined oxygen, so that the deoxidation is more complete than that obtained in the crucible during that period of melting which the Sheffield steel makers call "killing."

Cold Pig and Ore Briquettes.

Owing to the rather high price of pure scrap, we have in later years sometimes worked the furnace at Gysinge with cold pig iron and very pure iron ore briquette (made by the Gröndal process). In this case, as with cold pig iron and scrap, when using the electric furnace purely as a melting machine, without doing any refining, most of the different elements in the raw materials will be found in the steel except carbon and silicon, which naturally will be oxidized, and also dissolved or combined gases, the presence of which can scarcely be determined by analysis.

Analyses of Raw Material.

Herräng Pig Iron.

Phosphorus	0.009%
Sulphur	0.011%
Manganese	0.025%
Silicon	0.15%

Herräng Ore Briquettes.

Silica	5.50 %
Ferric oxide	85.93 %
Ferrous oxide	3.96 %
Alumina	0.76 %
Oxide of Manganese	0.63 %
Lime	2.23 %
Magnesia	0.97 %
Phosphoric acid	0.006%
Sulphur	0.01 %
Copper	0.007%
	100.003%
Metallic iron	63.16 %
Phosphorus	0.0026%

Physical Data.

I have not been able to detect any difference in quality between the steel made from pure pig iron and pure scrap, and steel made from pure pig iron and pure iron ore briquettes.

GENERAL DATA REGARDING MAKING STEEL FROM COLD PIG IRON AND COLD SCRAP, AND FROM PIG IRON AND IRON ORE BRIQUETTES.

Power Consumption.

The necessary theoretical power per ton of steel produced from cold pig iron and scrap is about 489 kilowatt hours.

The furnace at Gysinge consumed about 800 kilowatt hours per ton when working with cold pig iron and scrap. When cold pig iron and iron ore briquettes were used, the power consumption per ton of steel was increased about 50 per cent. The figure below is given by Dr. Engelhardt, in "Stahl und Eisen." The full drawn curve shows the power consumption in kilowatt hours per ton for different sizes of furnaces. The other dotted curve shows the calculated power consumption if the furnace is charged with molten pig and ore.

Cost of Production.

Power	Kroner	7:	= $1.88
Wages	"	6:50	= 1.75
Moulds, etc.	"	....	= ....
Cost of casting	"	4:	= 1.08
Flux	"	1:90	= .51
Lining and repairs	"	3:	= .82
Interest and amortisation	"	....	= ....
General expenses	"	5:	= 1.35
Total	"	27:40	= $7.39

Advantages of the Kjellin Induction Furnace.

The experience both in Sweden and in some of the large European steel works with the Kjellin furnace has proved it to be an excellent melting machine when it is a question of making the highest class of steel from pure raw materials, and that it, both technically and economically, can very easily compete with the old methods, especially with melting in crucibles, even when the power is generated by coal.

In the induction furnace the steel can be better protected against injurious effects than even in the crucible. It allows tappings which are very large compared with the contents of a

crucible, and the steel seems to be of even better quality than steel produced in crucibles from the same raw materials. The alternating current has a kind of stirring effect upon the steel, so that the contents of the furnace get thoroughly mixed. This stirring effect is quite visible to the eye, and sometimes it has been necessary to cut off the current in order to convince crucible steel makers that the steel was sufficiently killed and calm and that the movements on the surface of the molten steel arose only from the action of the current and were not caused by gases escaping from the steel. As the heat is created by a current passing through a bath with uniform cross section, the temperature of the whole bath is the same, and there is no risk that the steel is overheated in one part of the furnace while it might be too cold in another.

There is much which could be added, but Dr. Engelhardt has so fully gone into the subject in his articles in "Stahl und Eisen," 1905, and "Electrotechnische Zeitschrift," 1907, that I would have in great part to repeat his statements, and I will therefore content myself with giving a list of furnaces constructed after the original Kjellin type:

	Weight of charge		Kw. Capacity	
Röchling'sche Eisen & Stahlwerke, Völklingen	8,500	kilos	750	kw.
Fried. Krupp, A. G., Essen	8,500	"	750	"
Oberschlesische Eisenindustrie, A. G., Gleiwitz	1,500	"	180	"
Poldihütte, Kladno, Bohemia	4,000	"	440	"
J. Brauns' Söhne, Vocklabruck, Austria	400	"	65	"
Allg. Kalciumkarbid-Genossenschaft Gurtnellen (Switzerland)		"	330	"
Vidua de Urigoitia è Hijà, Araya, Spain	1,500	"	215	"
Alti Forni Gregorini, Lovere, Italy	1,500	"	330	"
Eisenwerk Domnarfvet, Gysinge, Sweden	1,500	"	175	"
Metallurgiska Aktiebolaget, Trolhättan, Sweden	2,000	"	300	"
Vickers Sons & Maxim, Sheffield	1,500	"	225	"
Gröndal Kjellin Co., Nine Elms Lane, London	100	"	60	"
	Experimental furnace.			
American Electric Furnace Co., Niagara Falls, U. S. A.	800	"	150	"
American Electric Furnace Co., Niagara Falls, U. S. A.	100	"	60	"

Of these furnaces, the one at Gurtnellen is not working now, because its situation made pure raw materials very expensive by reason of the high freight rates; the materials available in the vicinity were not suitable for the intended production of high class steel without previous refining. It is interesting to note that the Poldihütte furnace made about 2,000 tons of crucible

quality steel in their four-ton furnace during the last quarter year.

The 8½-ton furnace at Völklingen has been replaced by a furnace of the Röchling-Rodenhauser type, allowing of a convenient refining of the material.

II. The Röchling-Rodenhauser Electric Furnace.

The Fig. 2, which is taken from an article by Wedding, in "Stahl und Eisen," gives an idea of the principle of this furnace. In this figure H H signifies the two legs of the iron core of the transformer. Both those legs are surrounded by primary coils A connected with the alternating current generator. Through the action of the currents in the primary coils, secondary currents are induced in the two closed circuits formed by the bath. As will be seen from the figure, those two circuits are connected so that the whole looks like the figure 8.

The primary coils naturally are so arranged that the induced currents in the common part of the two circuits, that is, between the legs H H of the iron core, have the same direction.

So far the furnace acts like two combined ordinary induction furnaces. The difference consists in the use of extra secondary coils B B surrounding the primary coils A A. From those secondary coils the currents are conducted to metallic plates. Those plates are covered by electrically conducting mixture of refractory material G, which forms part of the lining of the furnace.

The currents from those secondaries then pass from the plates E, through the lining G, and then through the main hearth D of the furnace. The channels C only act as conductors for the secondary currents induced in the bath. In the main hearth D we then have the currents from the channels C C and also from the extra secondaries B B.

The currents from those extra secondary coils have a very useful influence on the electrical properties of the furnace.

Let us, for simplicity's sake, assume that each of the channels C furnishes one-fourth of the current through the main hearth D, and that consequently half of the current comes from the extra secondaries, and that the resistance of the main hearth is half of that in each of the channels C. The current in the main hearth after adding the extra secondaries being the double

of that directly induced, the energy in the main hearth will be four times that caused by the induced currents alone.

The ratio between the total energy transformed into heat in the main hearth and channels after and before the introduction of the extra secondaries will then be two to five.

The effect of this is a considerable increase in the power factor. If the current from the secondary did not increase the

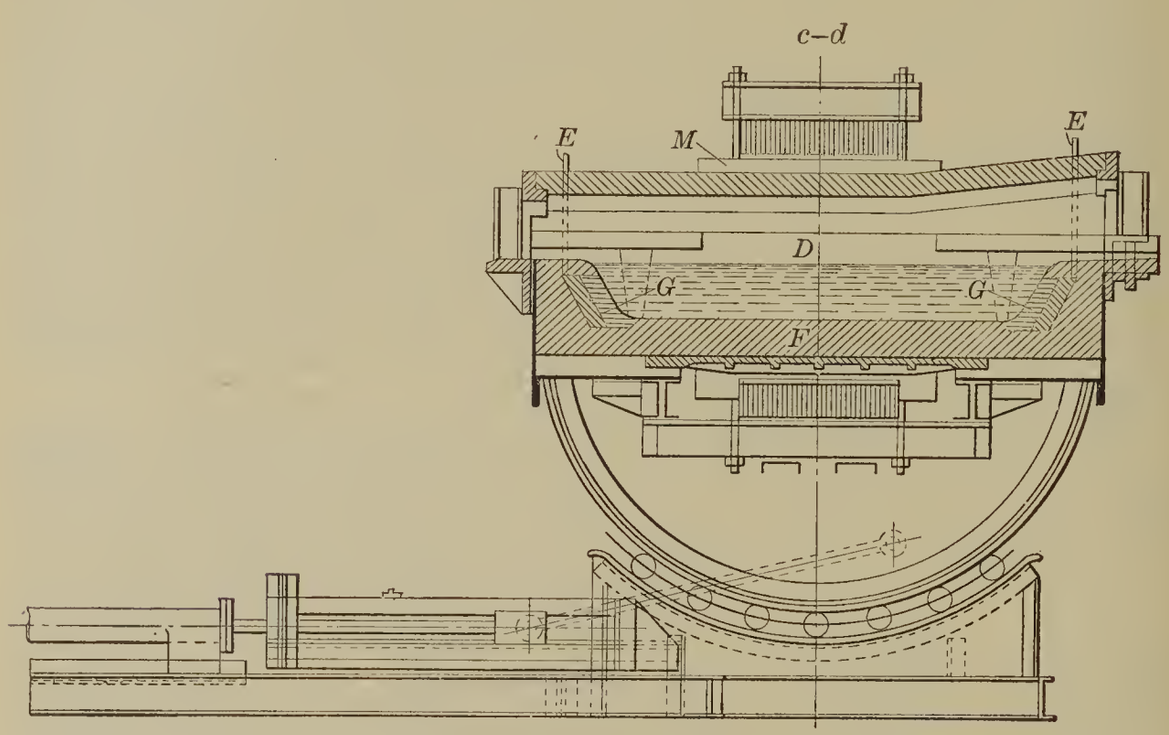


FIG. 2 (*a*).

self-induction, and the power factor of the furnace when worked only with the currents directly induced in the bath were, say, 0.50, the introduction of the extra secondaries would mean an increase of the power factor to 0.823. Another advantage with this arrangement is that the magnetic leakage field surrounding the primary coils, which formerly only had the effect of checking the primary current and decreasing the power factor, is now utilized for inducing currents in the extra secondaries.

The total result is that the main hearth can be made of much larger cross section than before, and that, nevertheless, a good power factor can be obtained even in big furnaces without the use of such a low periodicity of the current as was necessary with the original induction furnaces.

The amount of extra power that can be given to the furnace by means of the extra coils is of course not unlimited, because increased power means increased current, and consequently

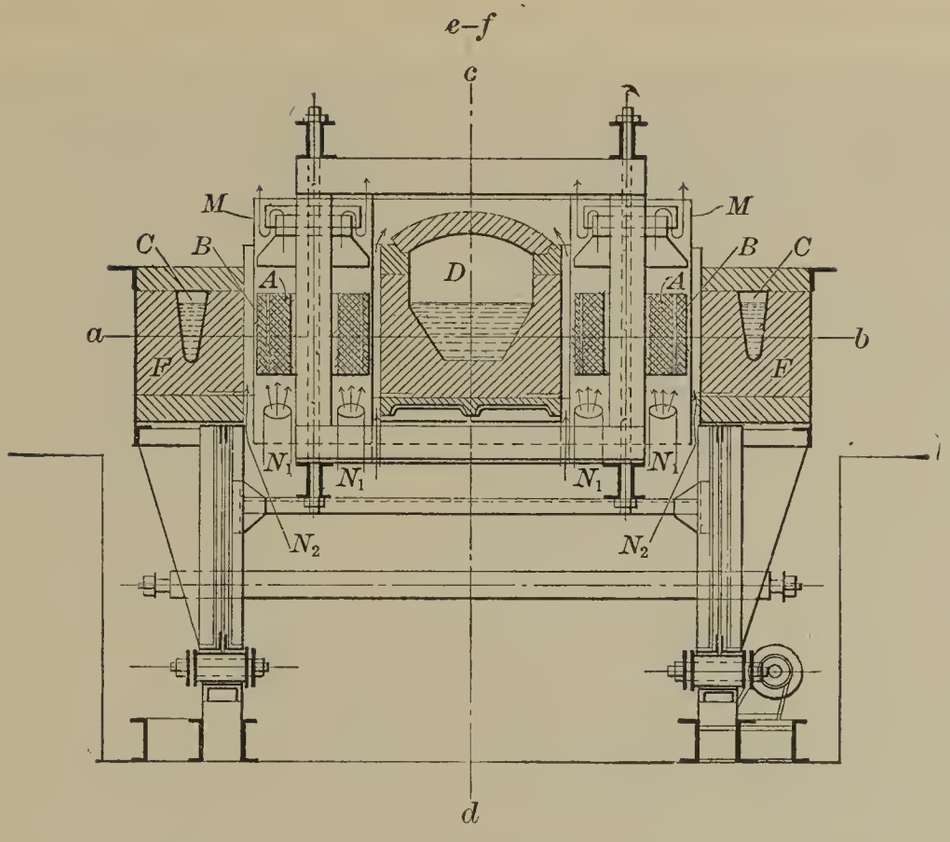


FIG. 2 (*b*).

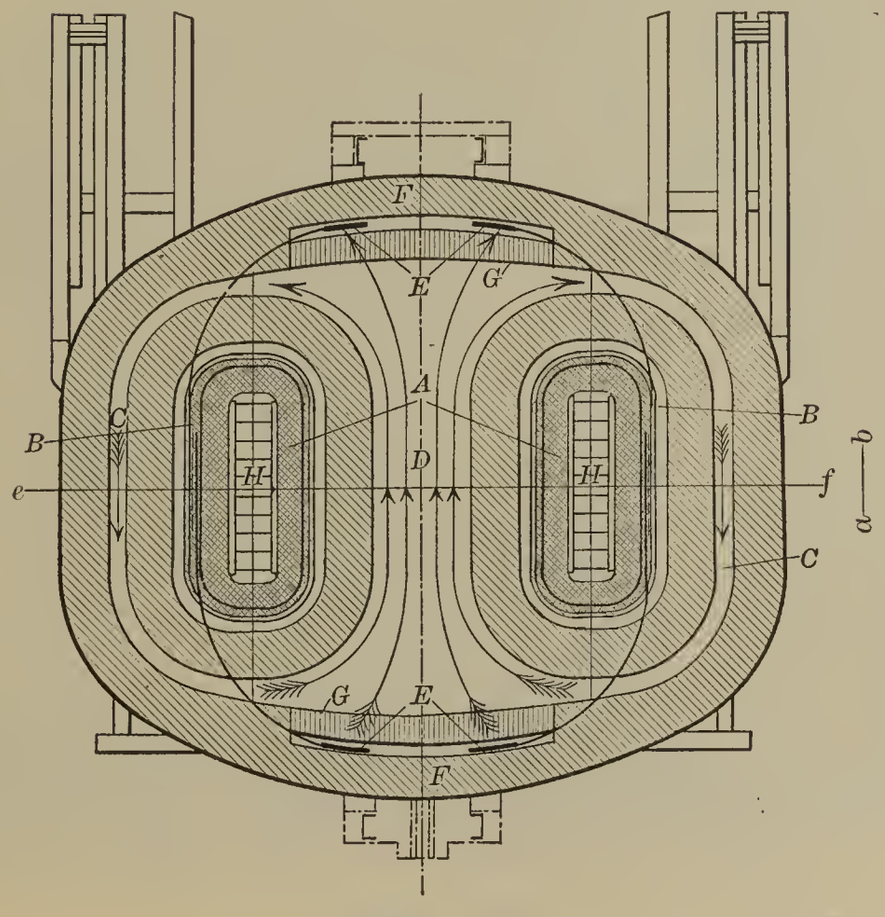


FIG. 2 (*c*).

increased current density in that part of the lining that conducts the current to the steel. This current density must not be driven too far, because the heat evolved when the current passes the lining will increase as the square of the current and too high a current density would therefore result in the destruction of the lining.

This is the reason why a combination of induced currents and currents taken from the extra coils must be used. It would not for the reason stated be possible to conduct all the amount of current necessary for the working of the furnace through the lining, not to speak of the pinching effect that would very probably cut off the current at the contact between the steel and the lining if the current density in the lining were driven too far.

As I mentioned before, the Röchling-Rodenhauser furnace was constructed for the purpose of using it for the refining of fluid Bessemer steel from the converter at Völklingen in order to produce a higher quality of rails than before, and also with the intention of going in for high class steel in general.

For refining purposes the furnace is worked in the following way:

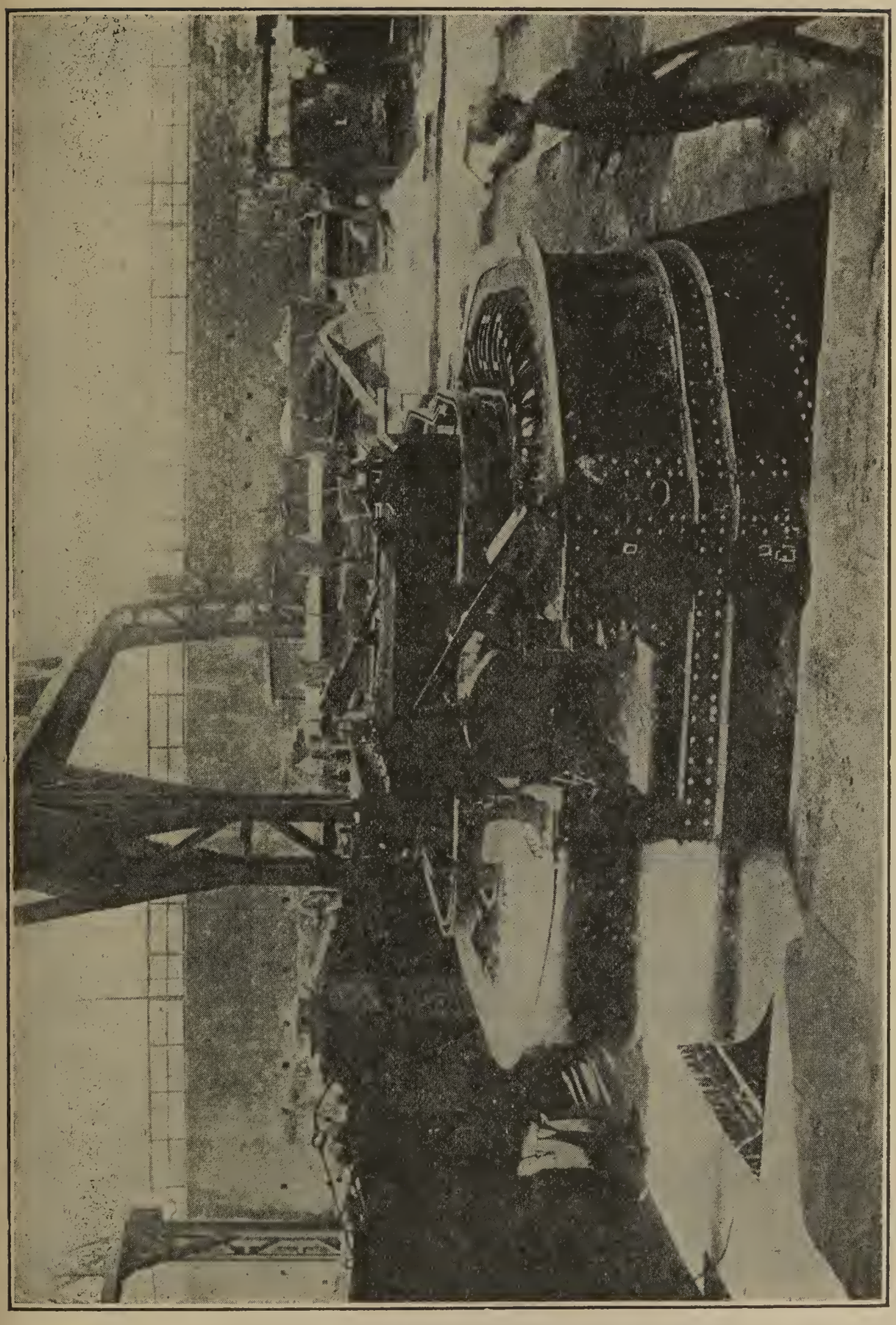
After tapping, fluid steel from the converters is poured into the furnace, and suitable materials—burnt limestone and mill scale—for forming a dephosphorizing basic slag are added. When the reactions are ended this slag is taken off by tilting the furnace. For making rails the phosphorus is brought down sufficiently low in one operation, but for the making of the highest class of steel the operation has to be repeated.

When the phosphorus is removed, the carbon in the steel (if carbon steel is made) is adjusted by adding pure carbon to the bath, and afterwards a new basic slag is formed in order to remove the sulphur. This slag is also formed of burnt lime, sometimes with the addition of fluxes such as fluorspar.

One necessary condition for successful desulphuration is that the slag is free from iron, and therefore sometimes ferro-silicon is added in order to quicken the reduction of the iron in the slag.

The first furnace of this type built at the Völklingen works was a 3.5 ton furnace, *i. e.*, the total content of the furnace was 3.5 tons. The power consumption and other details of the working of this furnace will be given below.

Trial charges for rail steel were made in this furnace, and,



ILLUS. 3:
Single-phase Röchling Rodenhauser Furnace at Völklingen.
8 Tons, 5 Cycles, 4,000 Volts, 700 Kw., Cos. φ 0.80.

the results being very satisfactory, the works secured orders from the Prussian Government railways for electro-steel rails, so that this furnace would be fully occupied for the production of rails. The intention being also to produce high class steel,

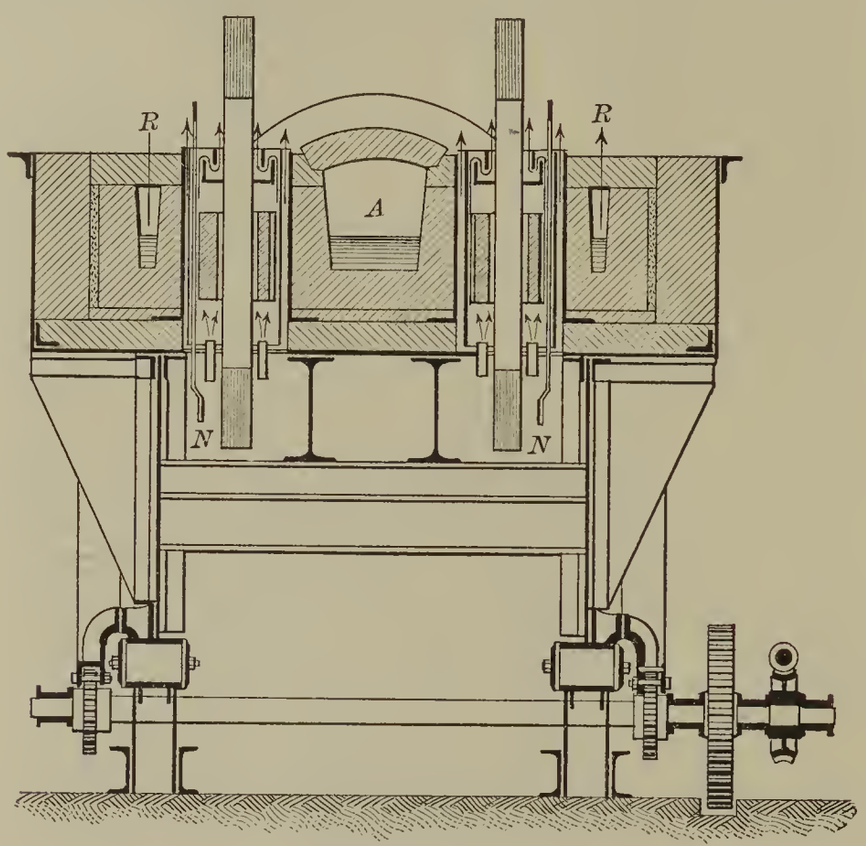


FIG. 3 (*a*).

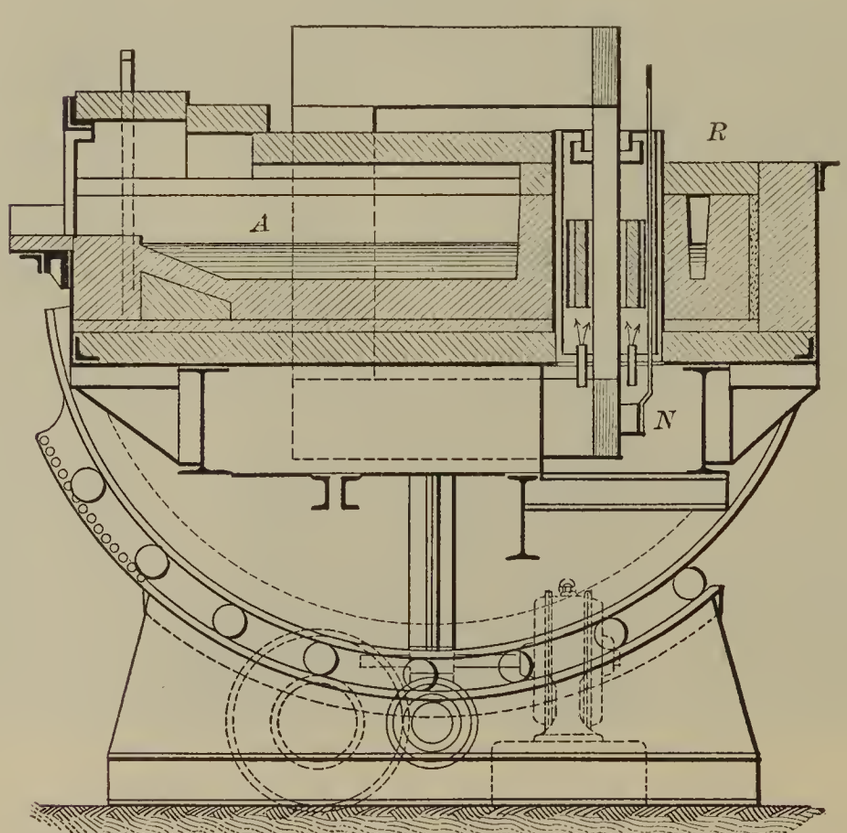


FIG. 3 (*b*).

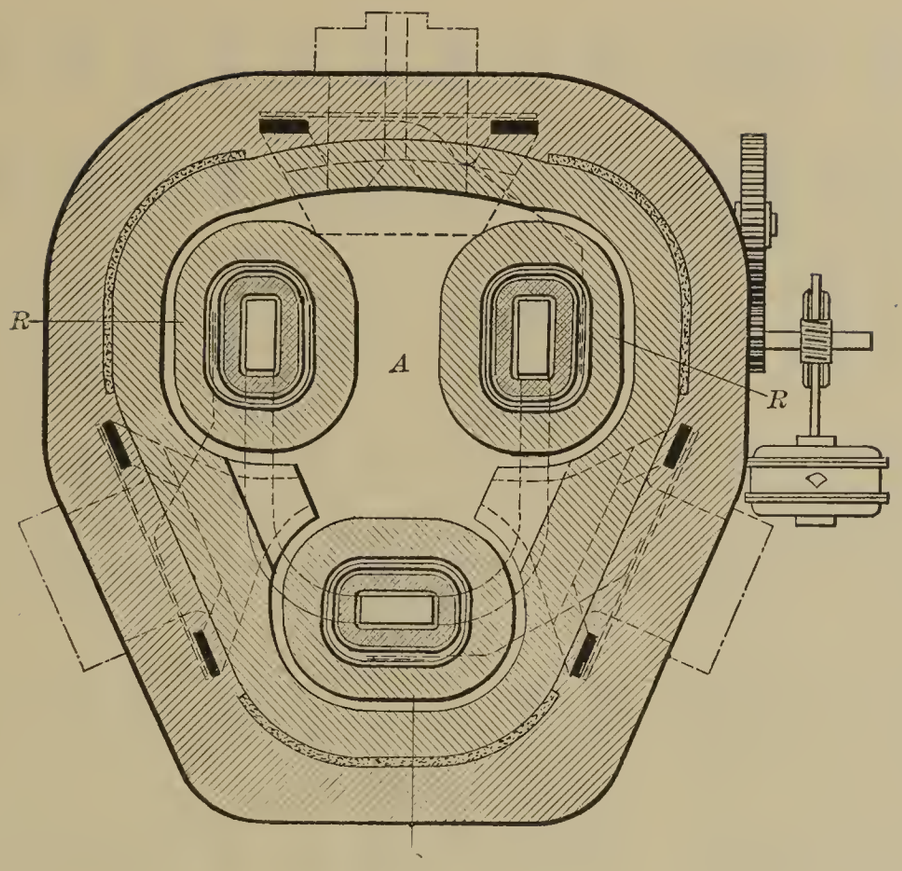


FIG. 3 (*c*).

it was found necessary to build another furnace for this purpose, and it was then decided to build this latter one for three-phase current. The reason for this was that by building a three-phase furnace the directly induced currents were distributed on three circuits instead of two, which means a considerable increase in the power factor and would allow of a 1.5 ton furnace being run directly from the main lines of the works with three-phase current of 50 periods, with a power factor of 0.75-0.80. The Fig. 3 shows the construction of this furnace as described by Professor B. Neuman, in "Stahl und Eisen," 1908, Nos. 33 and 34. The latest progress at Völklingen is the construction of a single-phase furnace with a capacity of about eight tons, which furnace was started last autumn.

The reason why this time the single-phase type was chosen was that the low period single-phase dynamo formerly used for the 8½-tons Kjellin furnace could then be used. This furnace, which, like the others, is of the tilting type, is now continuously working.

Analyses of raw materials and finished products, tensile tests, and power consumption for 3.5-tons Völklingen furnace are given in Table I.

TABLE I.

Report of Making Mild Steel at Röchlings Works.

No.		CHEMICAL DATA C.	P.	Mn.	S.	Si.	PHYSICAL DATA Kg per m/m 2 tons	Tons per sq. inch	Per cent. Elong.	Per cent. Contr.	ELECTRICAL DATA Time in Hours	Units per ton in Kw.	Total Units in Kw.
43	S.	0.075	0.080	0.527	0.129	0.018							
	F.	.....	0.030	0.594	0.069	.....	64.0	40.50	21.0	28.5	2 h. 40 m.	300	750
46	S.	0.086	0.087	0.651	0.097	0.018							
	F.	.....	0.018	0.310	0.077	0.016	37.3	23.62	36.5	69.2	1 h. 50 m.	245	613
92 Da	S.	.....	0.060	0.361	0.101	0.018							
	F.	.....	0.011	0.377	0.061	0.019	35.4	22.48	37.0	75.0	2 h.	240	600
92 Db	S.	0.069	0.058	0.590	0.085	0.022							
	F.	.....	0.008	0.328	0.048	0.017	36.8	23.31	35.5	66.7	2 h.	240	600
92 Dc	S.	0.067	0.047	0.590	0.077	0.020							
	F.	.....	0.006	0.295	0.048	0.019	37.1	23.75	35.0	63.9	2 h.	243	610
100	S.	0.061	0.060	0.426	0.089	0.018							
	F.	.....	0.014	0.295	0.070	0.023	34.5	21.83	35.0	71.4	2 h.	243	610
101	S.	0.072	0.053	0.558	0.081	0.016							
	F.	.....	0.018	0.328	0.065	0.016	34.2	21.67	39.0	75.8	2 h. 20 m.	270	675
116	S.	.....	0.062	0.820	0.065	0.024							
	F.	.....	0.015	0.361	0.044	0.018	35.2	22.24	36.0	67.0	1 h. 50 m.	200	500
129	S.	.....	0.054	0.720	0.065	0.012							
	F.	.....	0.018	0.361	0.055	0.021	36.0	22.78	37.0	67.8	1 h. 50 m.	258	645
132	S.	0.082	0.072	0.623	0.097	0.018							
	F.	.....	0.015	0.279	0.065	0.018	35.0	22.16	37.0	68.2	1 h. 55 m.	204	510

S.= Start. F. = Finish.

147	S.	0.053	0.622	0.101	0.026								
	F.	0.023	0.425	0.037	0.029	39.7	25.15	33.5	59.5	2 h.	20 m.	266	665
161	S.	0.049	0.566	0.077	0.020								
	F.	0.005	0.396	0.057	0.023	39.0	24.75	34.0	62.9	2 h.	40 m.	282	705
172 DI	S. 0.070	0.041	0.542	0.109	0.024								
	F.	0.004	0.301	0.068	0.029	36.8	23.31	34.5	62.1	2 h.	15 m.	224	560
173 DII	S. 0.070	0.045	0.512	0.060	0.020								
	F.	0.004	0.271	0.044	0.028	37.6	24.45	32.5	59.7	2 h.		197	492
176 DIII	S.	0.065	0.572	0.089	0.018								
	F.	0.007	0.271	0.078	0.021	36.5	23.15	35.5	63.6	1 h.	45 m.	175	438
199	S.	0.064	0.727	0.073	0.026								
	F.	0.008	0.253	0.065	0.034	35.2	22.24	34.5	66.0	2 h.		282	705
211	S. 0.084	0.049	0.569	0.102	0.018								
	F.	0.011	0.348	0.057	0.029	37.5	23.75	34.5	62.5	2 h.	5 m.	293	731
212	S. 0.092	0.095	0.474	0.089	0.018								
	F.	0.019	0.348	0.077	0.035	38.1	24.16	34.5	63.4	2 h.	5 m.	269	672
226 DI	S.	0.073	0.600	0.093	0.020								
	F.	0.004	0.284	0.053	0.021	35.2	22.24	35.0	71.2	1 h.	25 m.	212	530
227 DII	S.	0.061	0.695	0.089	0.024								
	F.	0.008	0.284	0.061	0.023	35.0	22.16	37.5	70.6	1 h.	55 m.	270	675
229 DIII	S.	0.073	0.569	0.085	0.016								
	F.	0.010	0.253	0.053	0.022	....	.....	....	....	1 h.	50 m.	230	576
230	S. 0.116	0.054	0.679	0.097	0.018								
	F.	0.028	0.695	0.048	0.122	57.4	36.35	26.25	51.3	2 h.	5 m.	282	705
240	S. 0.128	0.064	0.590	0.085	0.032								
	F.	0.020	0.618	0.065	0.140	40.0	25.32	33.0	66.8	1 h.	45 m.	235	587
241	S.	0.060	0.478	0.077	0.034								
	F.	0.011	0.309	0.053	0.018	37.5	23.75	38.0	69.6	2 h.	25 m.	274	685
254	S.	0.037	0.534	0.081	0.028								
	F.	0.005	0.307	0.057	0.022	36.7	23.25	37.0	66.8	1 h.	50 m.	250	628

Further details as to tests will be found at the end of this paper.

Table II.

Röchling-Rodenhauser Three-phase Electric Furnaces.

Contents Pounds	Electric Data				Tapping Pounds		Output per 24 hrs. lbs.	
	Kw.	Voltage	Cycles	Cos. ϕ	Cold Charging	Hot Charging	Cold Charging	Hot Charging
2,200	175	500	50	0.8	1,540	2,200	9,240	35,200
6,600	350	3,000	50	0.6	4,620	6,600	27,720	106,600
11,000	550	3,000	25	0.65	7,700	11,000	46,200	176,000
15,400	750	3,000	25	0.6	10,780	15,400	64,680	246,400

The weights given are calculated at 6 charges per 24 hours for cold melting and 16 charges for hot melting, whereas the actual times are 3½ hours per cold charge, and 1 hour 20 minutes per hot charge.

The voltage can be altered to suit circumstances, 12 per cent. to be allowed for regulation.

	P	S	Mn	C
Basic Bessemer steel charged into furnace having	0.08	0.08	0.5	0.1
Can be finished for rails, with 100/125 kw. hours per ton, to	0.05	0.04	0.8	0.5
Or, for "quality steel" with 300 kw. hours per ton, to	trace	trace	0.25	0.05

Open Hearth Steel:

Martin steel which has been previously refined, dephosphorized and desulphurized, containing about 1.22 carbon, 0.38 Mn. and 0.209 Si., has been put into the electric furnace, and allowed to remain there to remove gases, regulate the carbon content, and adjust the alloys, with an energy expenditure of 200/250 kw. hours per ton.

Table II gives all details regarding power, periodicity, power factor, production and cost of plant for different sizes of three-phase combined furnaces.

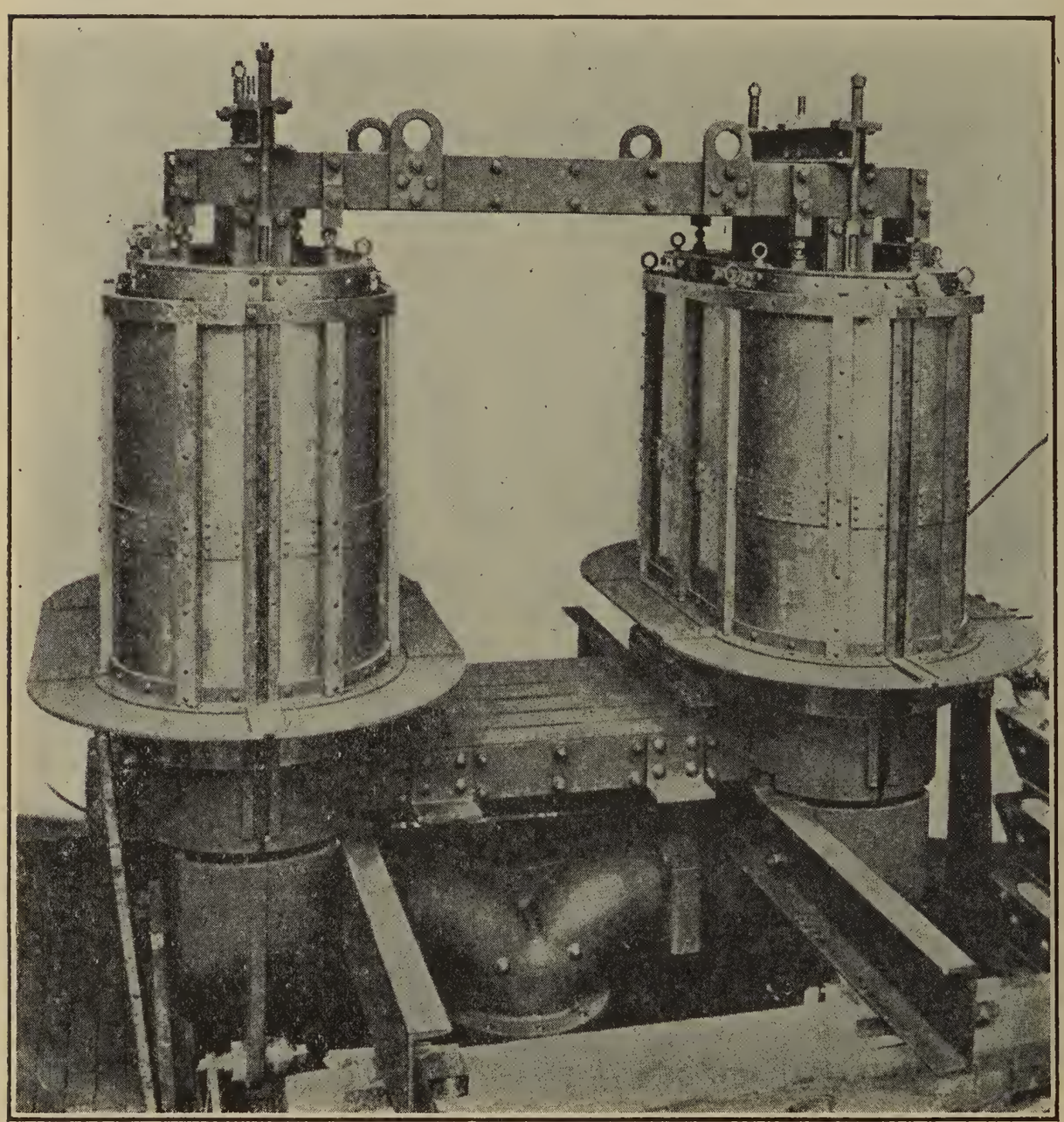
Based on the experience gained at Völklingen, the following costs of production have been calculated:

I. *Costs of production for a Two-ton Three-phase Furnace Producing Steel for Steel Castings.*

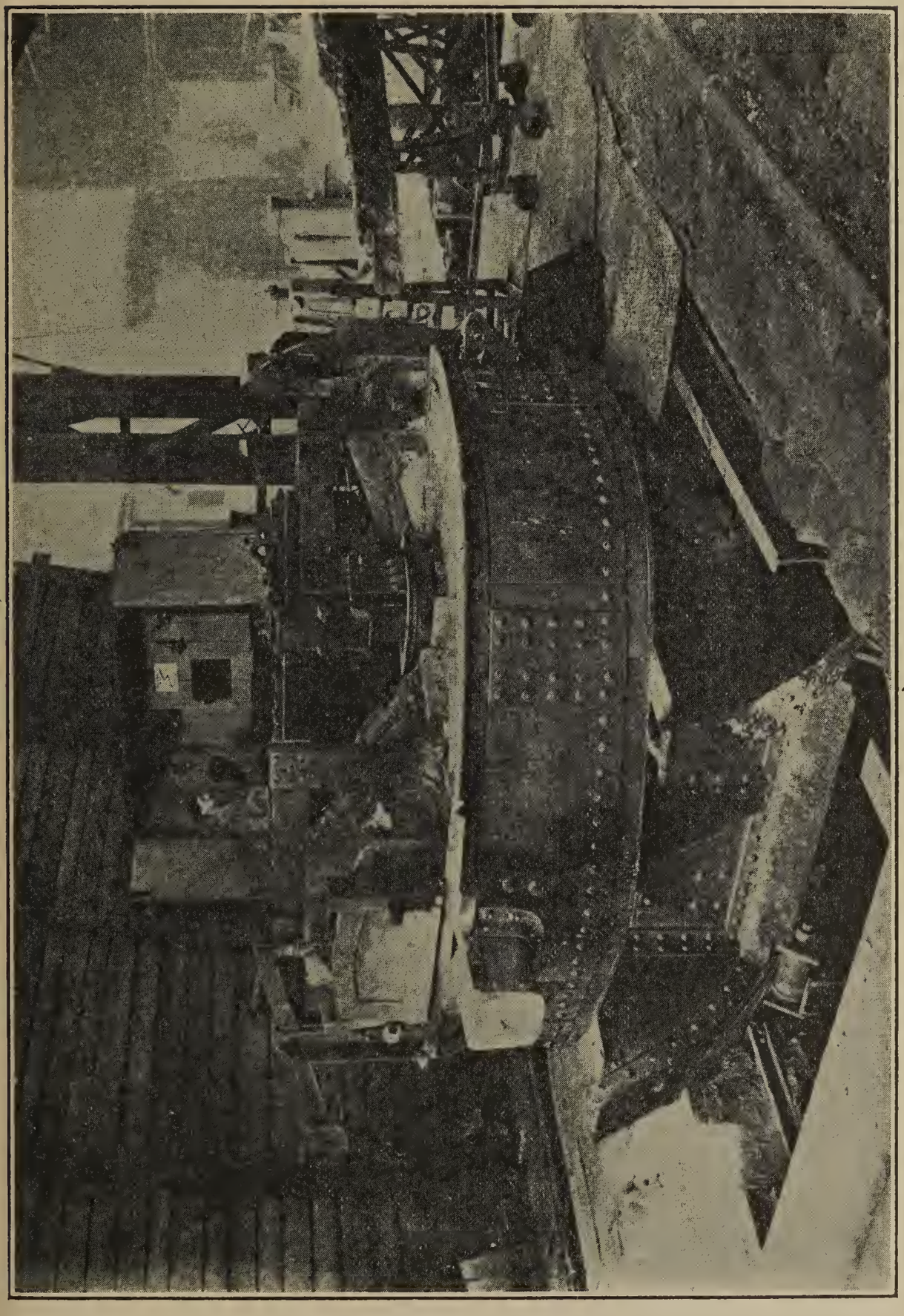
The raw material is fluid steel from the converters. The lower price is taken at 9 pfennig (2.18 cents) per kilowatt hour. The life of the lining is taken at 10 days, in which time 160 tons can be produced.

ILLUS. 4:
Furnace of Illus. 3, Tilted.

		Per ton steel.
Lining:		
Raw materials, 200 Marks	Mk. 1.25	$0.304
Wages	0.18	0.043
Heating up Furnace:		
2,000 kilowatt-hours, at 9 pf. for 160 tons steel, or	1.12	0.272
Refining:		
300 kilowatt-hours per ton, at 9 pf	27.00	6.52
Wages	1.75	0.425
Materials:		
20 kilos of mill scale, at 17 pf	0.34	0.082
30 " " lime, at 12 pf	0.36	0.087
6.5 " " ferro-silicon	2.00	0.485
4 " " ferro-manganese	0.88	0.214
Power for cooling arrangements	0.81	0.196
Repairs	0.80	0.194
Exchange taken at 20 Marks = $4.85.	Mks. 36.49	$8.822



ILLUS. 5:
Transformer for Single-phase Furnace at Dommeldingen.
3 Tons, 25 Periods, 380 Kw. 3,000 Volts, Cos. φ 0.40.



ILLUS. 6:
Röchling-Rodenhauser Furnace at Völklingen.
1.5 Tons, 3 Phase, 50 Periods, 500 Volts, 210 Kw. Cos. φ 0.8

To this must be added interest and depreciation of the plant. Taking 5 per cent. interest and 10 per cent. depreciation on 55,000 marks ($13,380), which will be the approximate cost of the plant, we get 8,250 marks ($2,000) per year, which for 300 working days would give 41.2 cents per ton, so that the conversion of the fluid product from the converters into high class steel, suitable for replacing crucible steel for steel castings, will cost 38.19 marks, or $9.23, per ton. For working the furnace three men are required. The time required for the removal of the lining is twenty-four hours.

II. *Production Costs for a Seven-ton Three-Phase Röchling-Rodenhauser Furnace.*

In this case the power is supposed to be generated with blast furnace gas engines, and the cost of power is taken at 0.03 francs, or 0.58 cents per kw. hour, or say $51.00 the kw. year.

Estimated working costs:

a—for rails or steels of like quality. *b*—for soft boiler-plate steel.
(Exchange taken at 25 francs = $4.85)

Original materials charged:

1,000	kgs.	molten Thomas steel, 80 fr. ton	$15.54	$15.54
20	"	limestone, 28 fr. ton	0.054	
30	"	" " " "		0.082
6.5	"	ferro-silicon, 300 fr.	0.378	0.378
5	"	ferro-manganese, 200 fr.	0.194	0.194
1	"	fluorspar, 26 fr.	0.005	0.005
10	"	rolling mill scale, 20 fr.	0.038	0.038
5	"	carbon, 40 fr.	0.038	
1,011.5	"	metals charged		
30.5	"	loss, or 3%		
981	"	product ..... Cost...	$16.247	$16.227
		Or, the original materials for the production of 1,000 kgs. cost	$16.56	$16.54

Power consumption (heating up):

The heating of a 7-ton, 3-phase furnace will require about 3,500 kw. hours. According to experience the furnace lining will stand 12 working days.

During this time there will be produced about 1,000 tons of rails, costing for power	0.020	
Or, about 500 tons of boiler plate, costing for power		0.04

Power consumption (refining):

125 kw. hours are required for rails, consequently the energy consumption for refining one ton is	$0.728	
250 kw. hours are required for refining soft boiler plate steel, at a cost of		$ 1.45

Power consumption (air blast):

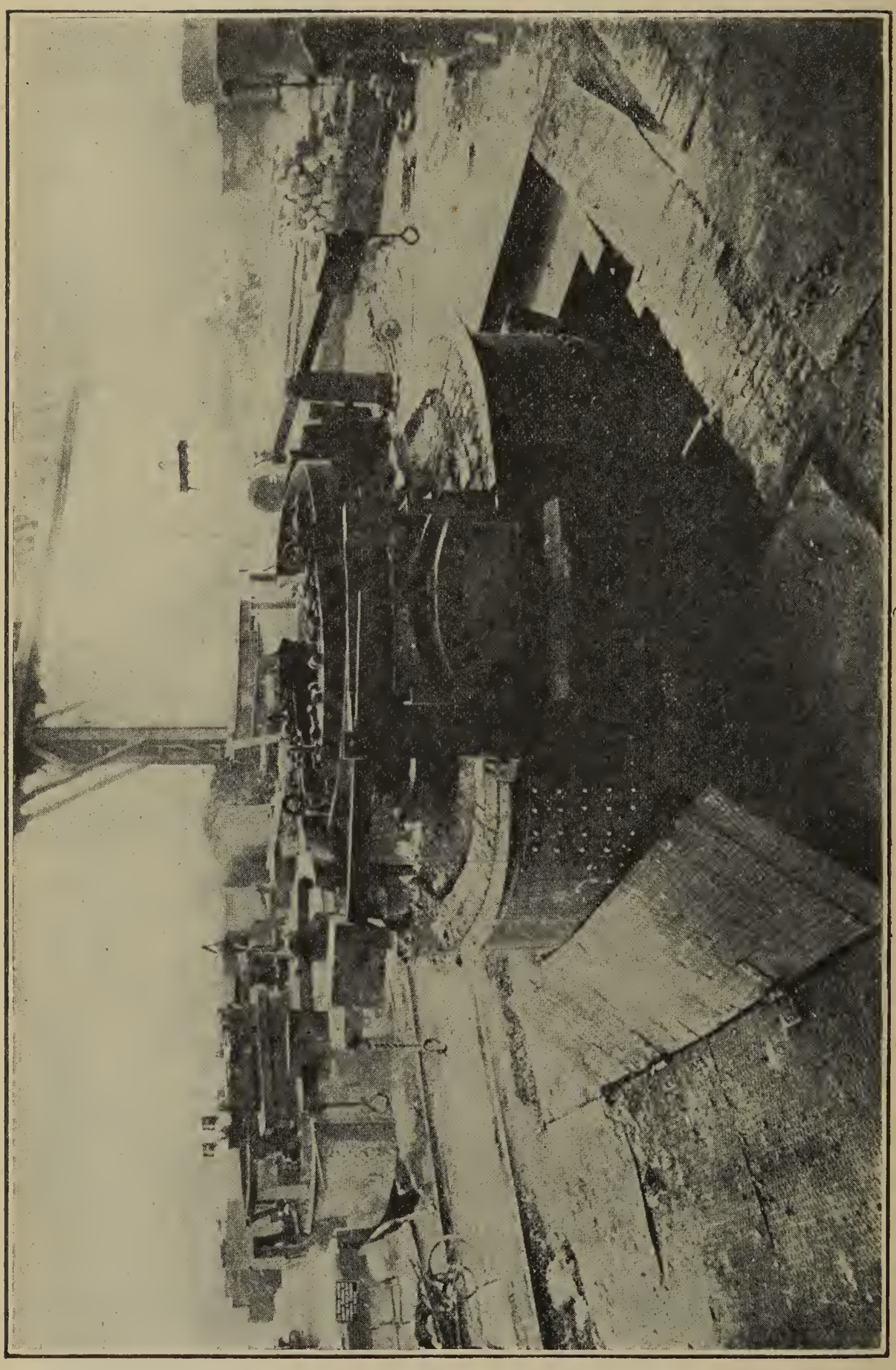
16.7 kw. are required for the fans, or approximately 400 kw. hours in 24 hours, or per ton of steel	0.029	0.058

Wages (24 hours):		
2 head melters, at 8 francs.....$3.10		
2 helpers, " 7 " 2.72		
2 laborers, " 5 " 1.94		
2 " on molds, at 4 fr..... 1.94		
2 " " crane, at 4.75..... 1.84		
2 electricians, at 5 fr..... 1.94		
Total wages $13.48		
As the daily production is about 84 tons of rail steel, or 42 tons of boiler plate steel, the above labor cost per ton is.....	0.16	0.32
Linings:		
2 foremen, at 6 frs.....$2.32		
6 laborers, tamping, at 4 frs..... 4.65		
$6.97		
Or, per ton produced, per lining.....	0.008	0.016
The ordinary laborers around the plant are used for working the pneumatic tamping machine.		
Lining materials:		
One lining costs when old materials are being used, for the 7-ton furnace, $72.10, therefore the cost per ton is.....$	0.072	$ 0.144
Amortization and interest:		
Cost of plant, about.....$25,600		
5% interest $1,280		
10% Amortization 2,560		
Or $3,840		
Supposing a yearly production of 22,680 tons of rail steel, or 11,340 tons of boiler plate steel, this item will be per ton.....	0.168	0.336

RESUMÉ.

Materials charged $16.56		$16.54
Power:		
Heating up	0.02	0.04
Refining	0.728	1.45
Wages:		
On furnace	0.16	0.32
On linings	0.008	0.016
Lining materials	0.072	0.144
Tools	0.097	0.097
Repairs	0.194	0.194
Amortization and interest.....	0.168	0.336
Licenses	0.582	0.582
Or, per ton of steel.....$18.62		$19.78

Besides having the same advantages as other induction furnaces, the Röchling-Rodenhauser furnace also allows of a convenient refining and a thorough elimination of phosphorus and sulphur. How far this refining will have to be carried, naturally



ILLUS. 7:
Another View of 3-Phase Furnace of Illus. 6.

depends on the quality of steel wanted. By repeated refining operations with fresh slag, the phosphorus and sulphur can be brought down to an exceedingly low percentage, but then the refining, of course, takes longer time and consequently more electric energy per ton of finished product.

Furnaces for large charges can without difficulty be worked with alternating currents of the periodicities now commonly in use for other purposes.

There seems not to be the slightest doubt but that furnaces of much larger type than the present eight-ton furnace at Völklingen can be built, and I think that the next step will be the erection of a 15-ton furnace.

This type of furnace has now been so thoroughly tested in continuous work that there is no doubt about its reliability.

The 3.5-ton furnace was worked continually for a whole year, almost all the time producing steel for rails, and more than 5,000 tons of rails have been sold from Völklingen to different customers at profitable prices.

The eight-ton furnace at Völklingen, since it commenced work in November last, has been running an average of thirteen to fifteen days on each lining, the output varying from 500 to 600 tons of high grade steel to 1,200 tons of rail steel to one lining. As this plant is now turning out in the neighborhood of 600 tons of rail steel per week, the assertion that these furnaces are not running commercially may be considered as effectually answered.

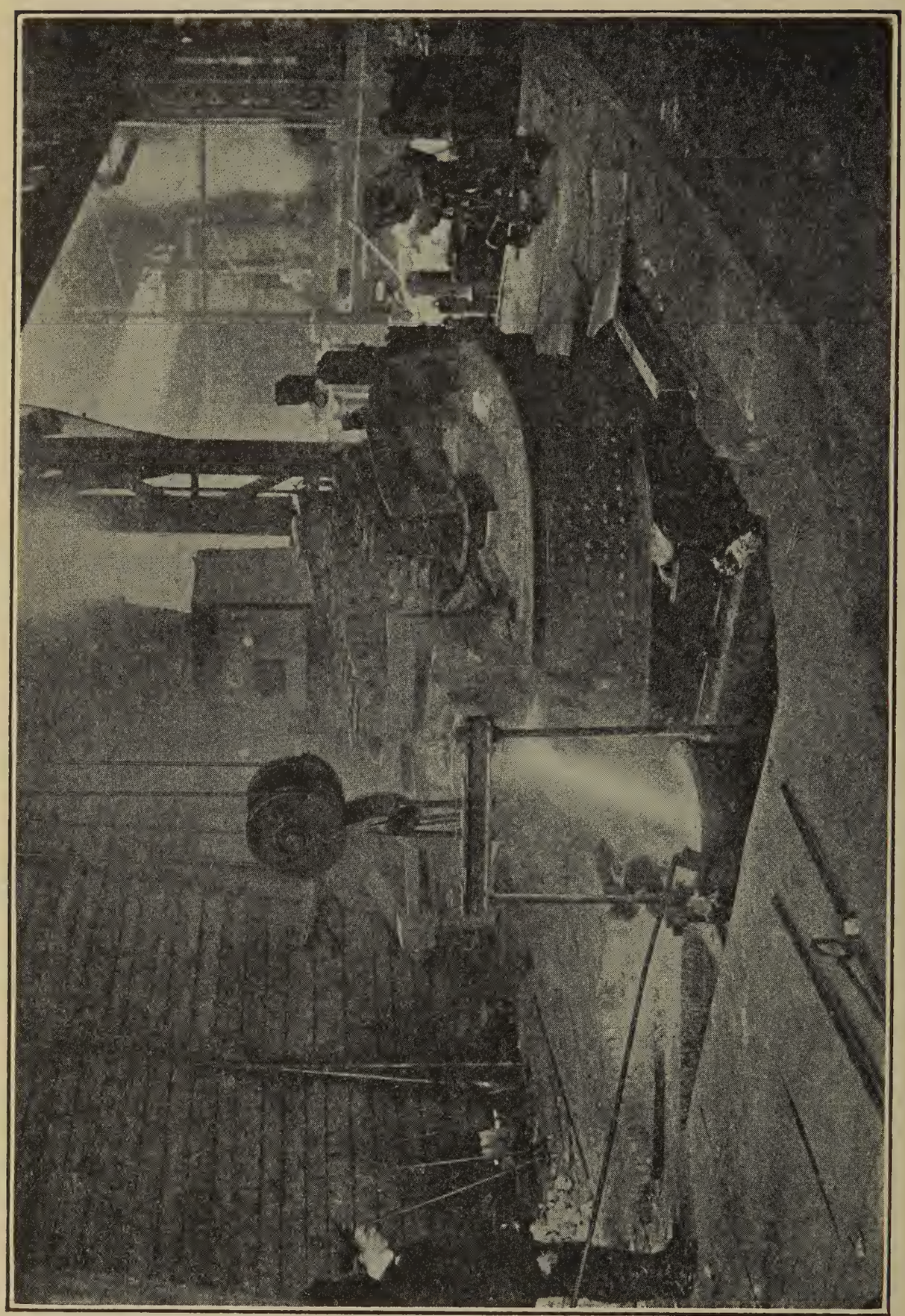
Electric Furnace Steel Rails.

For some time past steel made in a Röchling-Rodenhauser electric furnace has been manufactured into rails of standard section No. 8 for use on the United Prussian State Railway. Some data concerning these may be of interest.

Specifications for Electric Steel Rails.

The administration of the State railway has drawn up specifications with reference to electric furnace steel rails, particularly as to physical qualities and resistance to wear, as follows:

Tensile strength for track rails, a minimum of 70 kilograms per square mm., or about 99,000 pounds per square inch.



ILLUS. 8:
Tapping a 1.5 Ton, 3-Phase Furnace at Völklingen.

For point or switch rails, 75 kilograms per square mm., or about 160,000 pounds per square inch.

For ordinary basic Bessemer, or Thomas rails, a tensile strength of 60 kilograms per square mm., or about 85,000 pounds per square inch, is stipulated.

Elongation, in the case of electric steel rails, a minimum of 10 per cent., determined on samples 200 mm. (about eight inches) between marks.

Drop tests specify 80 mm. minimum bend (about 3 3-16 inches) on a bar one meter (39.37 inches) between supported ends, with a falling weight of 1,500 meter-kilograms (about 10,800 foot pounds).

Guaranteed life of track rails, ten years; of point rails, seven years.

Some data has been supplied by Mr. Herman Röchling, giving test figures for some charges of electric steel rails, and ordinary Thomas steel rails, which will be given at the end of this paper. The following, Table III, being the mean of six charges of electric furnace rails, and 16 charges of Thomas rails, will show the main differences:

TABLE III.

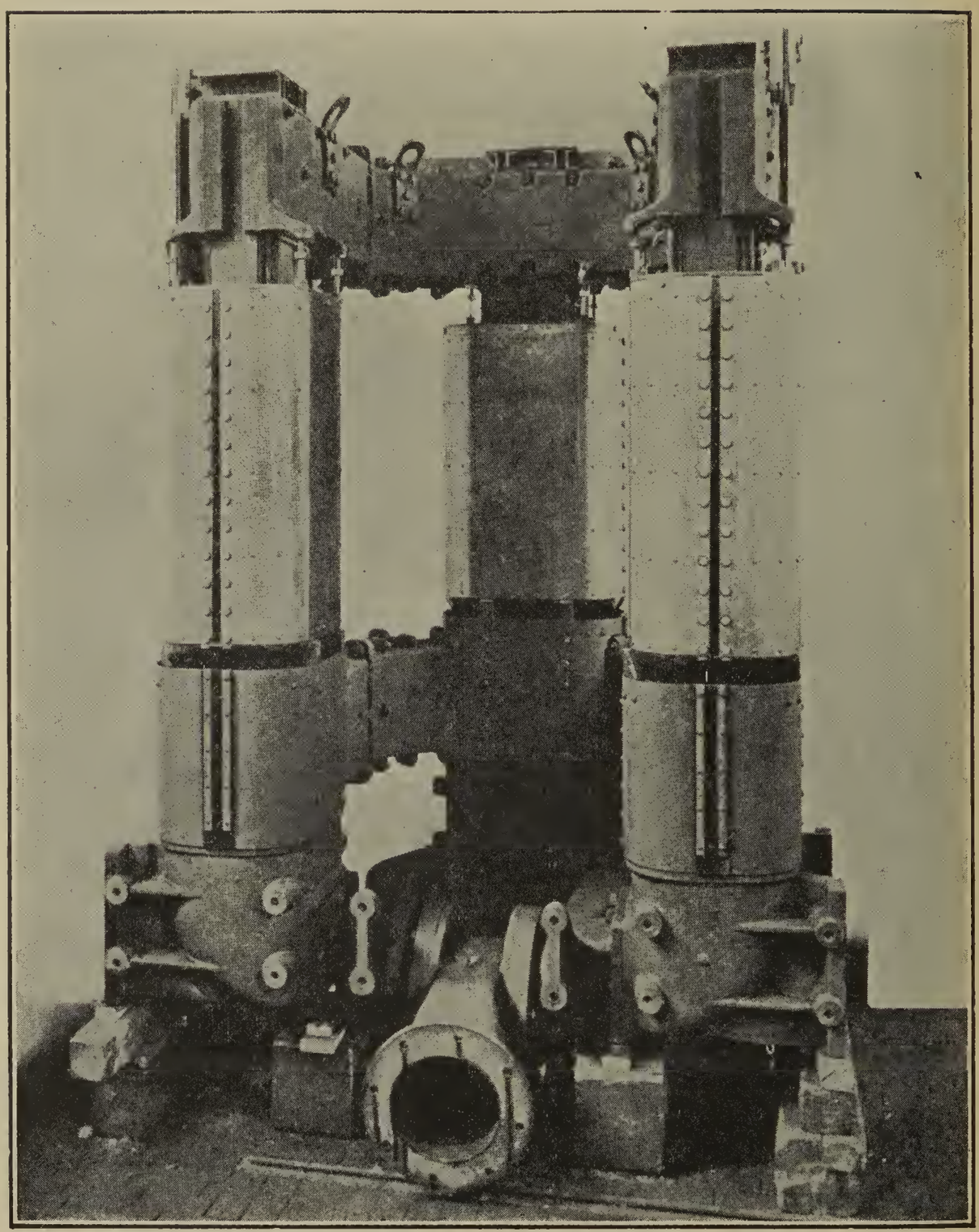
	C.	P.	S.	Mn.	Si.	Tensile strength lbs. per sq. inch	Elongation Per cent.	Contraction Per cent.
Electric Steel	0 54	0.056	0.042	0.984	0.21	119.000	15.4	24.1
Thomas Steel	0.36	0.073		1.127		97.000	17.6	26 2

The details of a number of physical tests will be printed with this paper, while the following concluding remarks may be quoted from a Völklingen report, dated 18th February, 1909:

"The tests, the results of which are given in the annexed report on material supplied, were carried out on electric steel rails section 8, which we have up to the present supplied to the Prussian Government."

"The elongations of the samples are determined at a distance between the marks of 200 mm."

"The ball pressure tests were carried out according to the stipulations of the Prussian Railway. The high elongation



ILLUS. 9:
Transformer for 3-Phase Furnace at Dommeldingen.
2 Tons, 50 Periods, 500 Volts, 275 Kw. Cos. φ 0.7

figure as compared to the comparatively high tensile strength figure is striking. The drop tests executed have given quite extraordinary results. When striking at 1,500 meter-kilos, at least six blows (charge, 550) were needed in order to obtain the bend of 80 mm. of a bar one meter long between supported ends, whereas for the charge No. 613 as much as eight blows were required. When testing the charges Nos. 522 and 632, the piece of rail submitted to the drop test after having obtained a bend of 80 mm., was to be broken by a blow of 4,000 meter-kilos. However, the result was that the two test pieces, upon being subjected to the blow, bent at respectively 126 and 123 mm. without breaking, and they could only be broken by putting the rails once more under the falling block and submitting to further blows."

"The composition of the rails is similar to that of the ordinary Thomas steel rails, only the higher carbons corresponding to the higher tensile strength (minimum 99,000 pounds per square inch) which is specified. The favorable result of the electric steel rails as compared to the Thomas rails can only be obtained through the 'killing' of the material in the electric furnace, under a slag which facilitates the deoxidation and the escape of the gases."

Refining From Crude Pig Iron.

At Dommeldingen very impure pig iron was charged into an induction furnace of the Röchling-Rodenhauser type, and refined as follows:

	Analysis of Charge	Analysis of Cast
Carbon	4.0%	0.5 %
Phosphorus	1.8%	0.025%
Sulphur	0.2%	0.03 %
Manganese	0.0%	0.76 %
Silicon	1.0%	0.056%

MECHANICAL RESULTS.

Breaking strain	95,000 lbs. per square inch
Elongation	20%
Contraction of area	36.33%
Duration of conversion	5 hours

In conclusion I desire to express my best thanks to Dr. Victor Engelhardt, Mr. Hermann Röchling and Mr. W. Rodenhauser for their kindness in placing at my disposal valuable information on the above subject, and for the permission to publish same.

Addendum.

An electric steel rail, made for the Metropolitan Railway of London, and tested at the Clarence Steel Works of Dorman, Long & Co., Ltd., contained carbon 0.78, silicon 0.196, manganese 0.285, sulphur 0.035, phosphorus 0.022. By the Brinell hardness test, with a 19-mm. ball and 50 tons pressure, it gave an impression 3.7 mm. in diameter. With a 2,240-pound drop test, falling 25 feet, it gave 3.56 inches deflection; second fall of 21 feet did not break it, but broke at the third blow with 37-foot fall.

The following results have been obtained from some 80-pound electric steel rails rolled in the United States, carbon content 0.80 per cent.

Weight of tup, 2,000 pounds. Distance between bearings, 4′-0″.

No. of Drop.	Height of Drop.	Total Deflection in Inches.
1	20′-0″	2.5
2	10′-0″	3.5
3	10′-0″	4.2
4	10′-0″	Broken.

A paper presented at the Fifteenth General meeting of the American Electrochemical Society, at Niagara Falls, Canada, May 6, 1909, President E. G. Acheson in the Chair.

THE SELF-CIRCULATING GIN FURNACE FOR THE ELECTRIC MANUFACTURE OF STEEL.

By Gustave Gin.

(*Translated by Jos. W. Richards.*)

I. The Gin Induction Furnace.

In induction furnaces, with uncovered canal, it is difficult to get uniform distribution of the heat and of the refining reactions, because of the small heat conductibility and slow diffusibility of the melted material. Much improved results are obtained by securing a continual circulation of the melted matter, which mixes all parts thoroughly and renews continually the reacting surfaces.

This object has been attained by Schneider in the furnace described in his U. S. Patent 761,920, and by Gin in his U. S. Patent 875,801. Our furnaces contain receptacles for the metal alternately in sumps and narrow passages connecting these, inclined and completely filled with metal. The whole forms a closed circuit in which the ascensional movement in the inclined connecting passages produces a continuous circulation of the entire liquid charge. The figures show the furnace which we have worked out with Messrs. Schneider and Co., and which is to be constructed at Essen by the Gessellschafft Friedrich Krupp. Figs. 1-4.

The furnace has two principal receptacles, *a* and *b*, united by the heating canals *c*. The vessel *a* is larger than *b*, and is called the working bath; it carries a tap door *e* for slag and a tap hole *f* for steel. The induction bobbins *d* surround the two heating conduits *c*, and are cooled by forced ventilation. The whole furnace is mounted on an axle, so as to tilt it for running off slag and metal.

It is easily seen why this form of furnace gives better results than an uncovered canal induction furnace. The heating is uni-

form in all parts of the furnace, and a very high temperature can be attained without fear of the "pinch" phenomenon in the heating passages. All parts of the melt come surely and rapidly into contact with oxidizing slag, giving quicker refining.

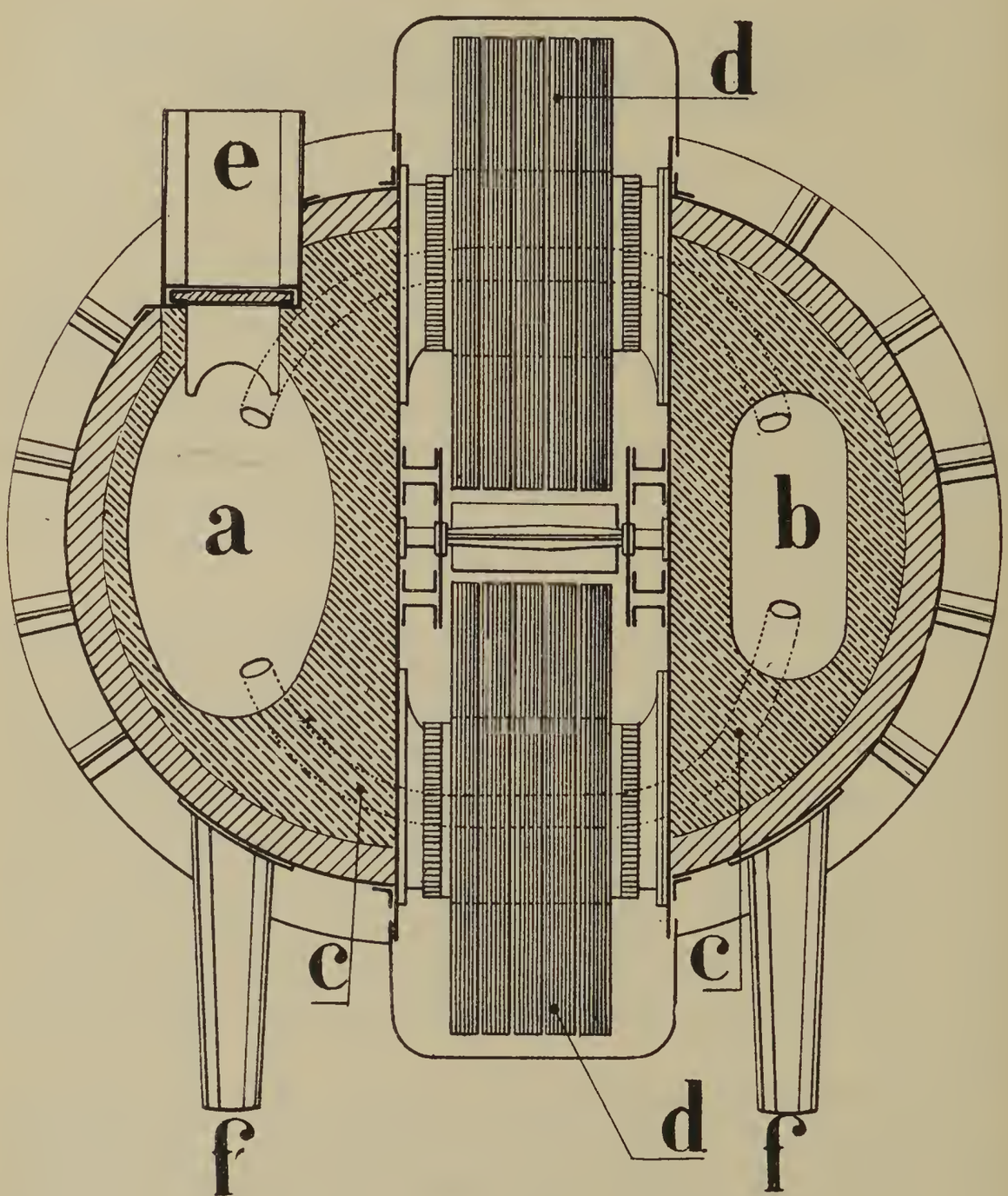


Fig. 1: Plan.

The velocity of circulation in the filled canals varies according to their inclination and diameter, but is so arranged as to be at least 40 cm. per second.

It is known that in induction furnaces with annular canal the

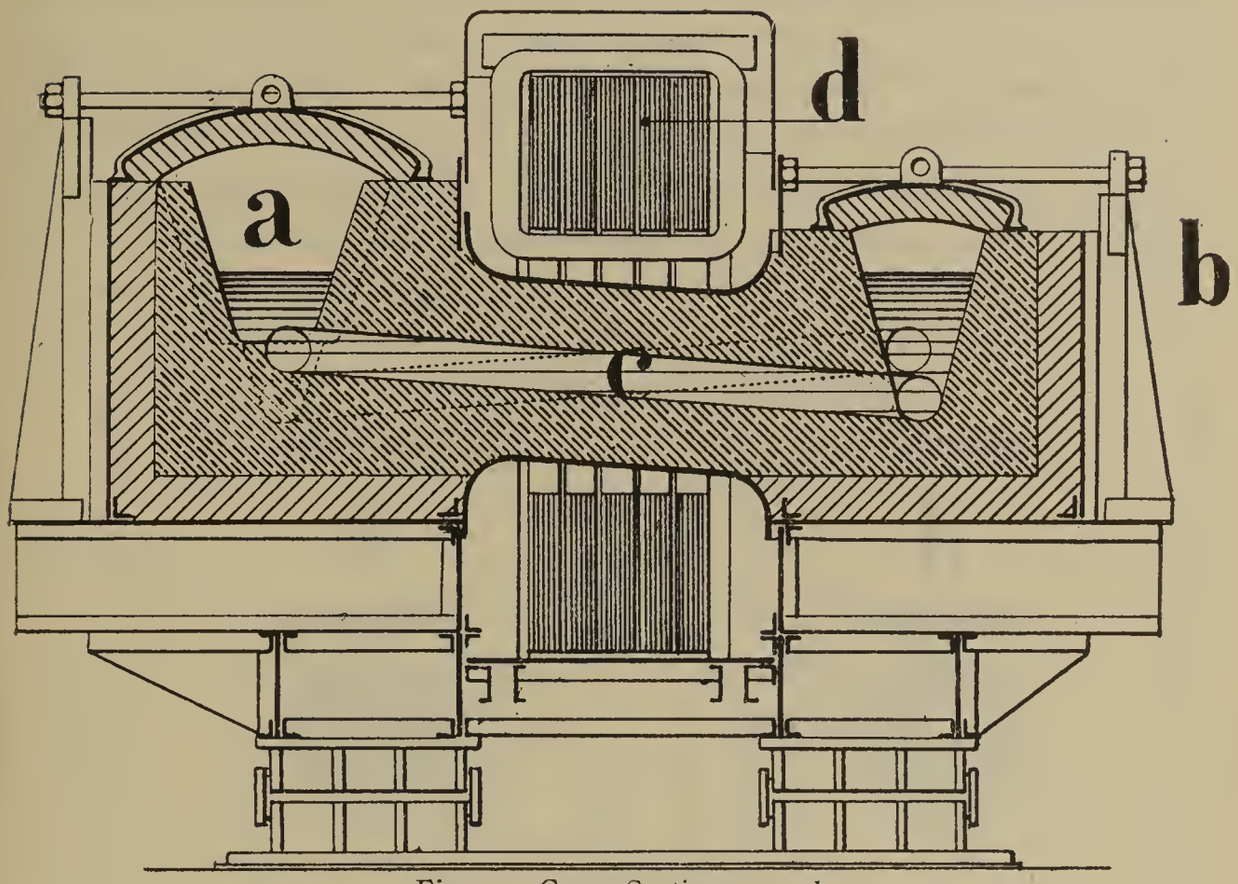


Fig. 2: Cross Section on *a b*.

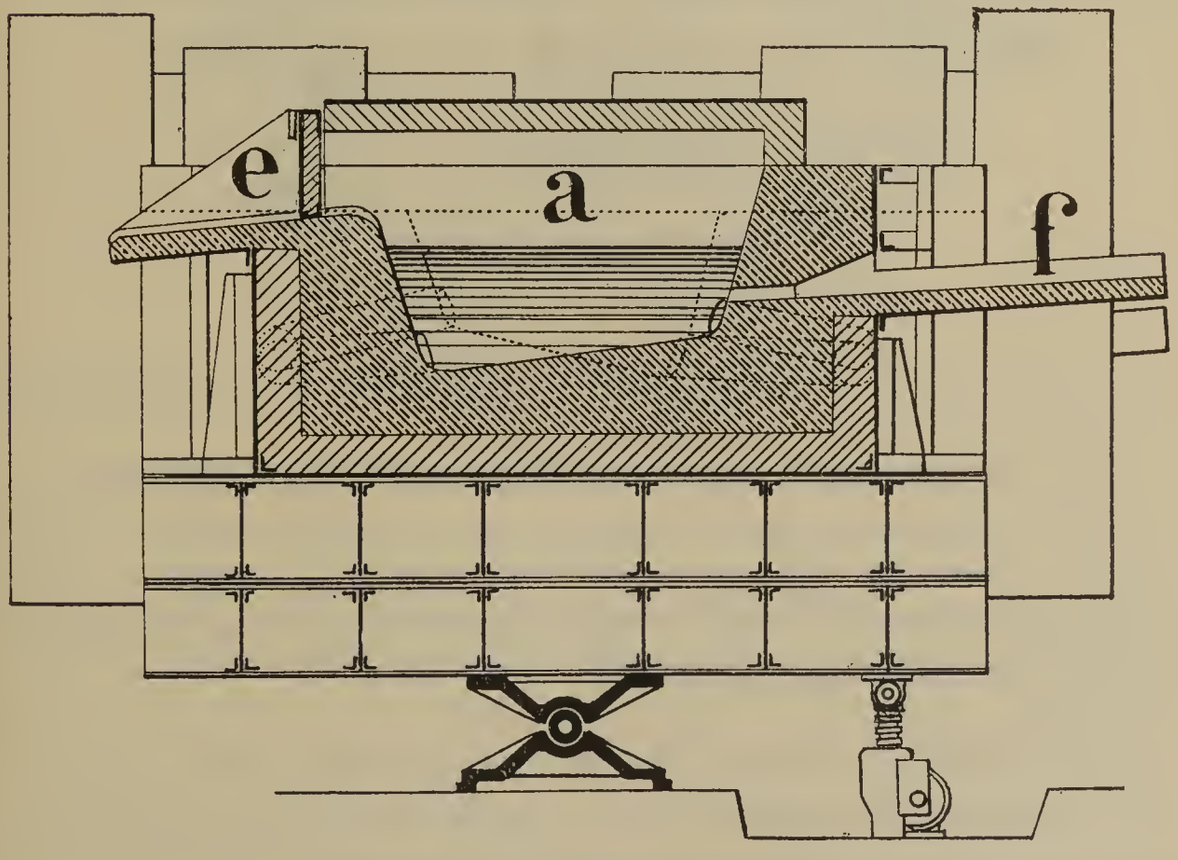


Fig. 3: Section on *a e*.

coefficients of self-induction and of mutual induction increase with the size of the secondary circuit and with the power of the furnace, necessitating diminishing the frequency of the inducing current, and leading to generators and inductors of enormous dimensions, weight and cost. With the self-circulating furnace under discussion, the ohmic resistance of the circuit may be increased without simultaneously exaggerating the self-induction or mutual induction, permitting the operation of furnaces

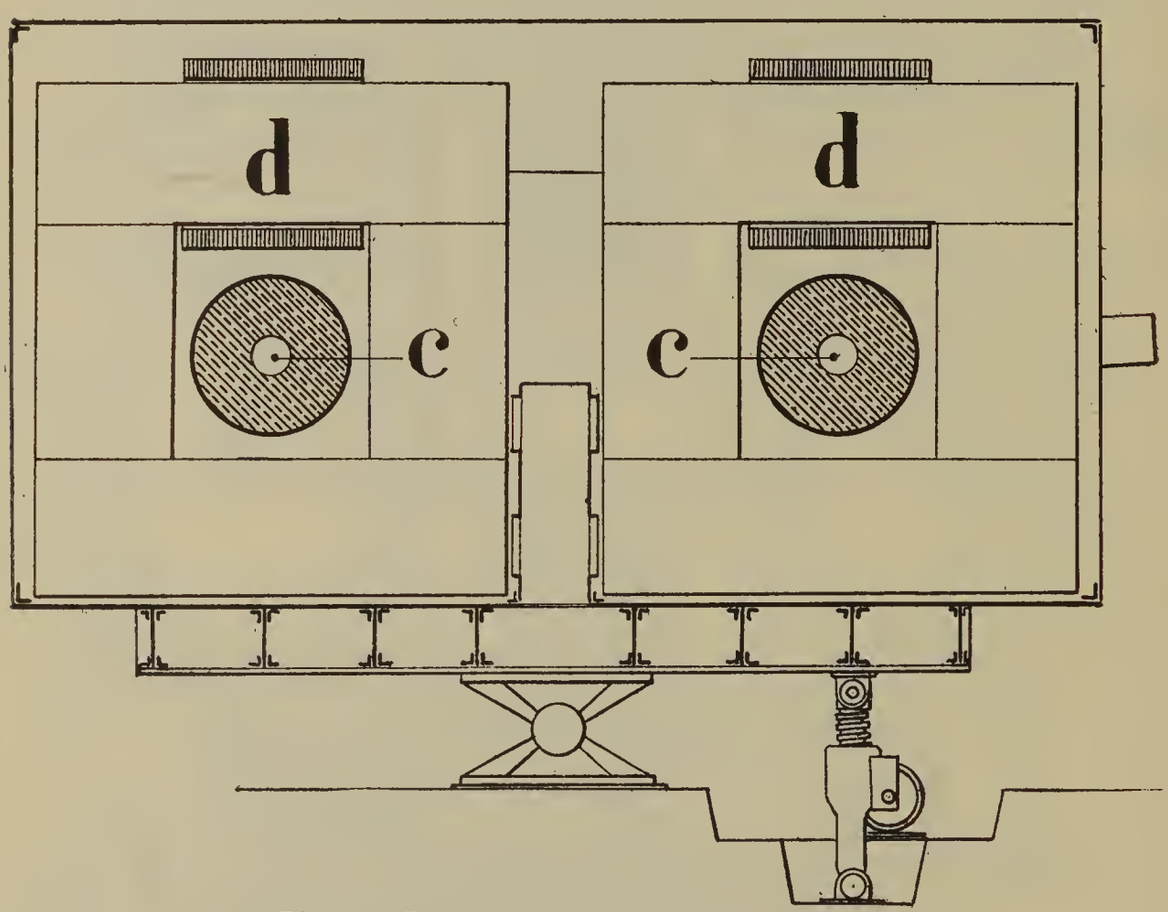


Fig. 4: Section on the Induction Cores, *d d*.

with satisfactory power factor with generators and transformers of normal frequency, weight and price.

The correctness of this conclusion can be judged from the practical calculation published in our accompanying paper. The furnace shown in Figs. 1 to 4 is constructed for 420 kw. The primary current is at 4,800 volts, frequency 5 periods per second. Metal cast, 5 tons per heat.

II. Gin Electrode Furnace With Self-circulation.

In one type of electric steel furnaces, electric arcs pass from one or more electrodes to the bath to be heated.

If the current passes from two movable electrodes to the bath as an intermediary, supporting two arcs in series, the heating is very superficial, heating the slag to a high temperature, but heating incompletely and non-uniformly the bath of metal.

If the current from a single electrode passes to the bath and then away from it by a conductor hearth, there is heat developed

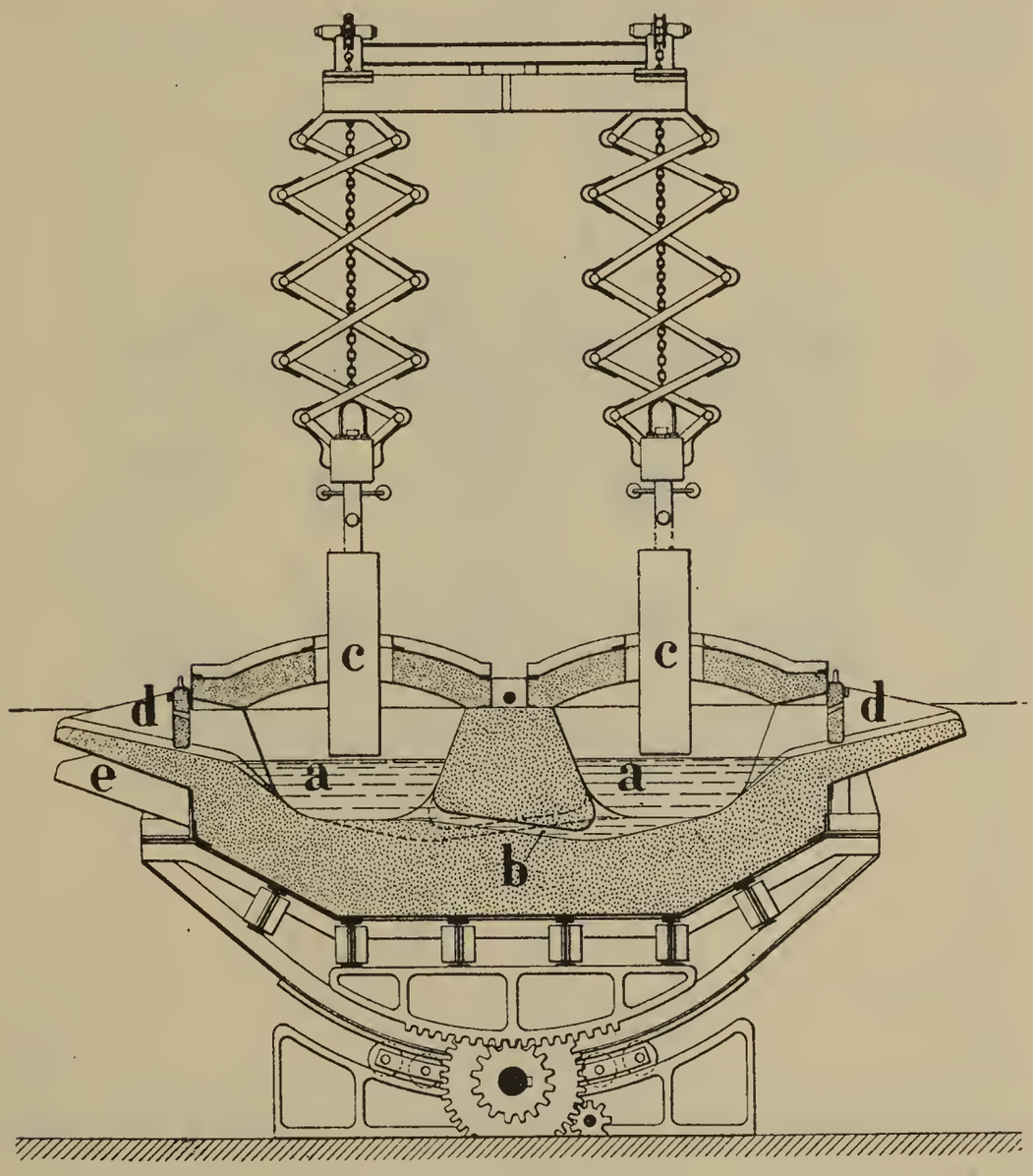


Fig. 5.

in the metal proportional to the electric resistance of the mass thus traversed by the current. But with melted iron, a relatively good conductor, this quantity of heat is practically negligible, and the useful effect is again reduced to the superficial heating produced by the arc jumping to the surface of the bath.

In both the above cases the heating is defective and the thermal

efficiency low, for the heat conductibility of liquids is small, and one can use for heat circulation in them *only those currents produced by sub-surface heating of the deeper parts of the bath.* We make use of this principle in our induction furnace by the inclined canals entirely filled with metal, which are entirely submerged. The same principle can be utilized in an electrode furnace.

The simplest application is shown in Figs. 5, 6 and 7, in

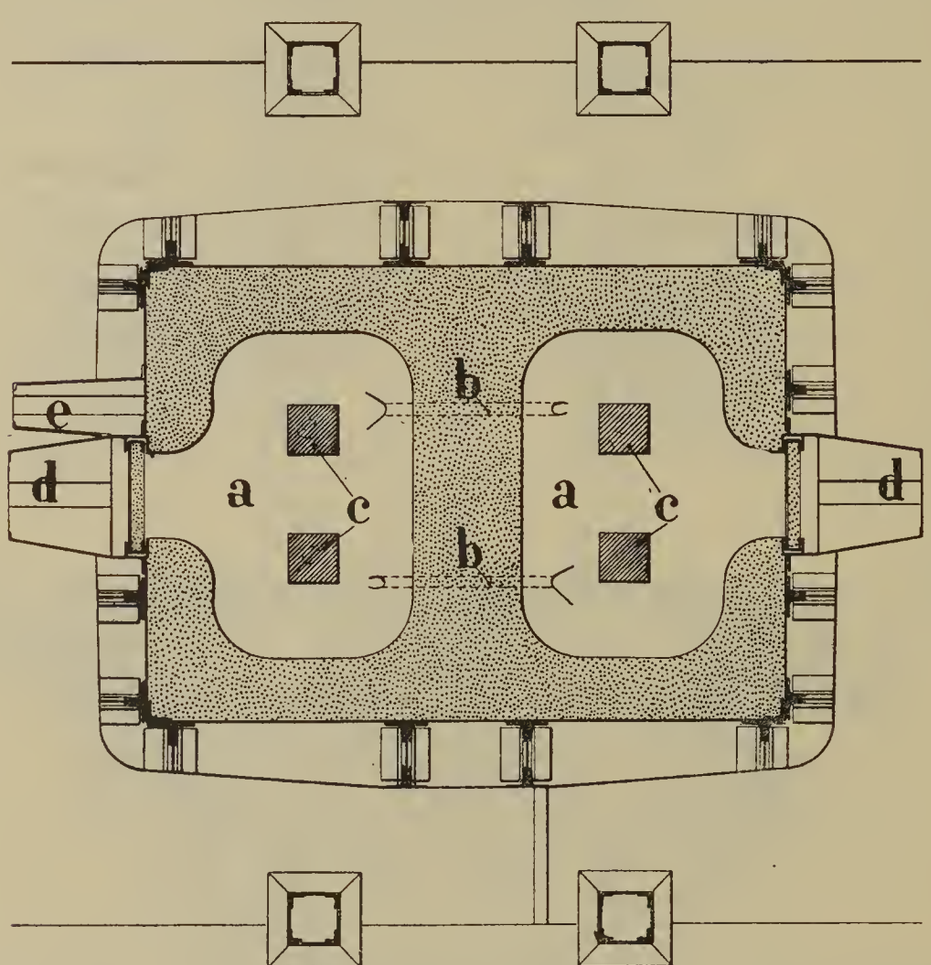


Fig. 6.

which the furnace has two reservoirs *a,* united by the tubes *b,* inclined in opposite directions. The electrodes *c* are in communication with the two reservoirs *a.* The current passes through the tubes *b,* causing heating and circulation beneath the surface, and from one reservoir to the other.

In similar manner a furnace can be operated on a tri-phase circuit, as shown in Figs. 8 and 9, by uniting three reservoirs, a_1, a_2 and a_3, by inclined heating and circulating canals *b,* the metal circulating continuously in one direction. Electrically, the

electrodes *c* and the canals *b* form a triangular group, in which the charge on each phase can be regulated by raising or lowering each of the electrodes *c*.

We have worked out the details of furnaces on this system for 750, 1,500 and 2,500 kw., furnishing at a cast 8, 14 or 20 tons of steel.

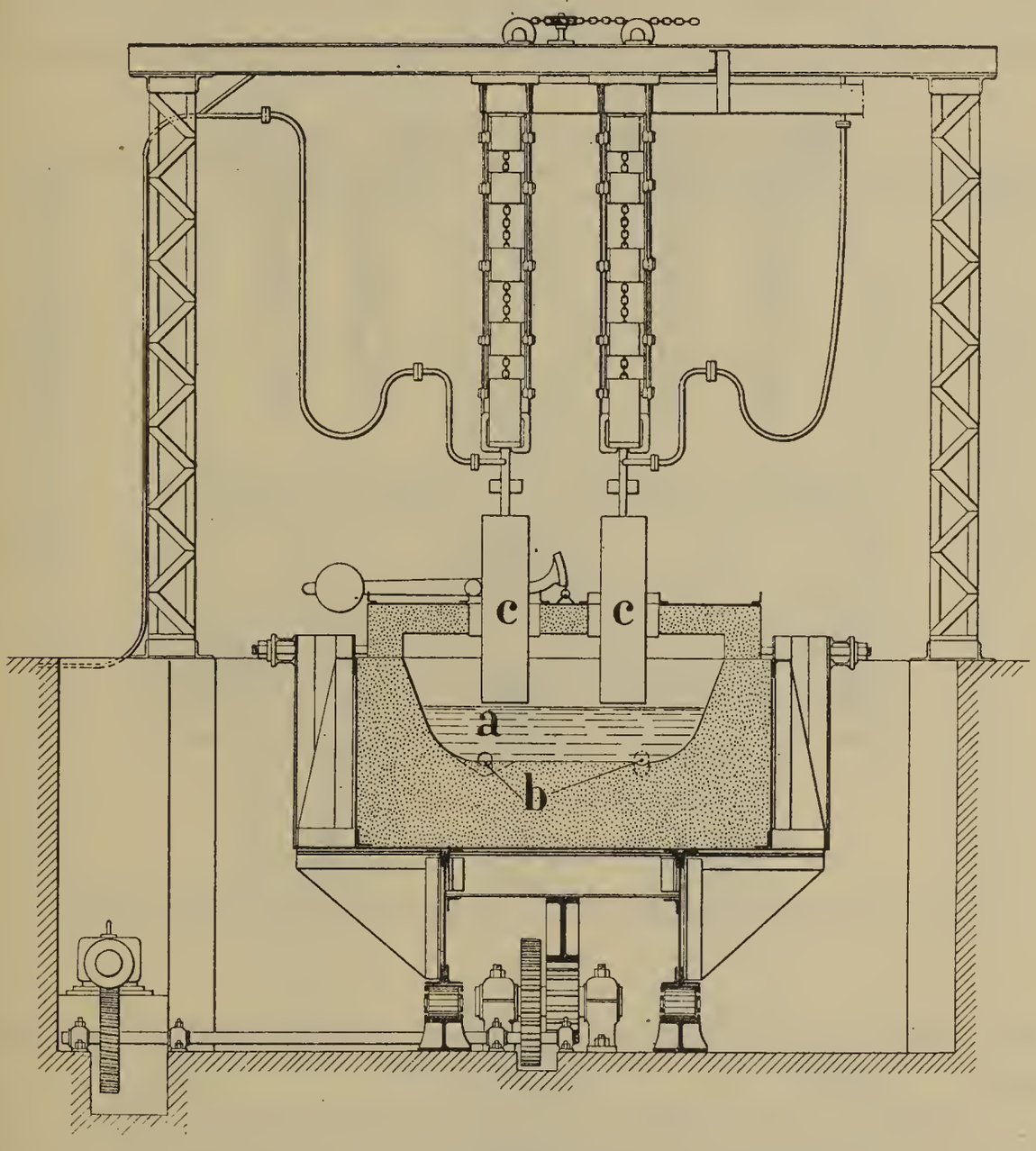


Fig. 7.

III. Gin Combined Self-circulating Induction and Electrode Furnace.

It may be expedient to combine the electrode and induction heating when making steel from materials carrying much impurities. In such case the large amount of slag covering the

bath offers a large electric resistance, and if the heating is by induction only, the heat is developed almost entirely in the metal, and the slag is insufficiently heated for keeping it properly fluid and active. To remedy this the slag may be otherwise heated by some supplementary means.

In the French Patent 339,010 of the Société Schneider & Cie., one or several pairs of electrodes are shown dipping into the laboratory of the furnace and furnishing additional heating by

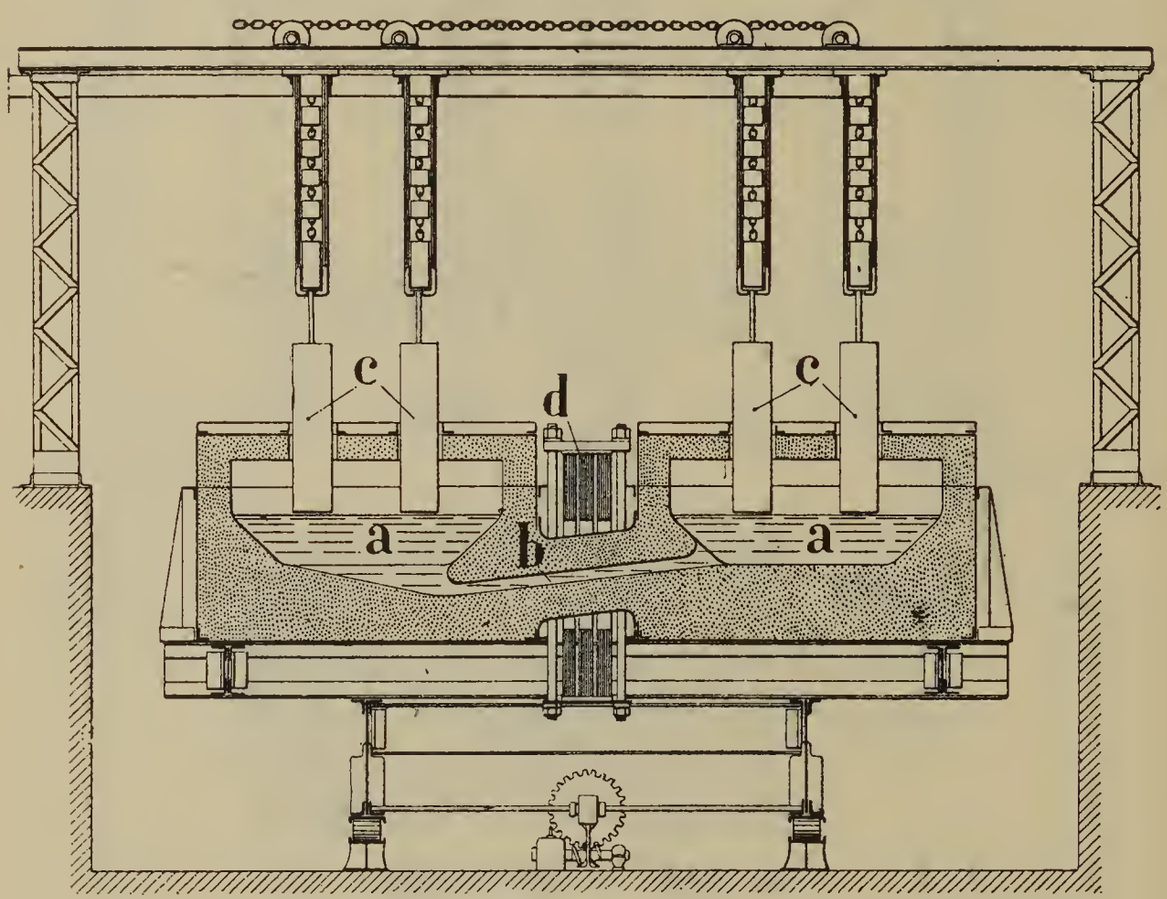


Fig. 13.

arcs passing between these electrodes or between them and the bath.

In the German patent application, D. R. P. 22,716, of the Roechlingsche Eisen und Stahlwerke zu Rodenhauser, is described the superposing upon the electromagnetic system of an induction furnace of a special secondary winding, which allows sending into the fused bath a second current, by the use of electrodes embedded in the walls of the furnace.

The two inventions above give an insufficient practical result, for they do not allow for or permit the simultaneous regulation of

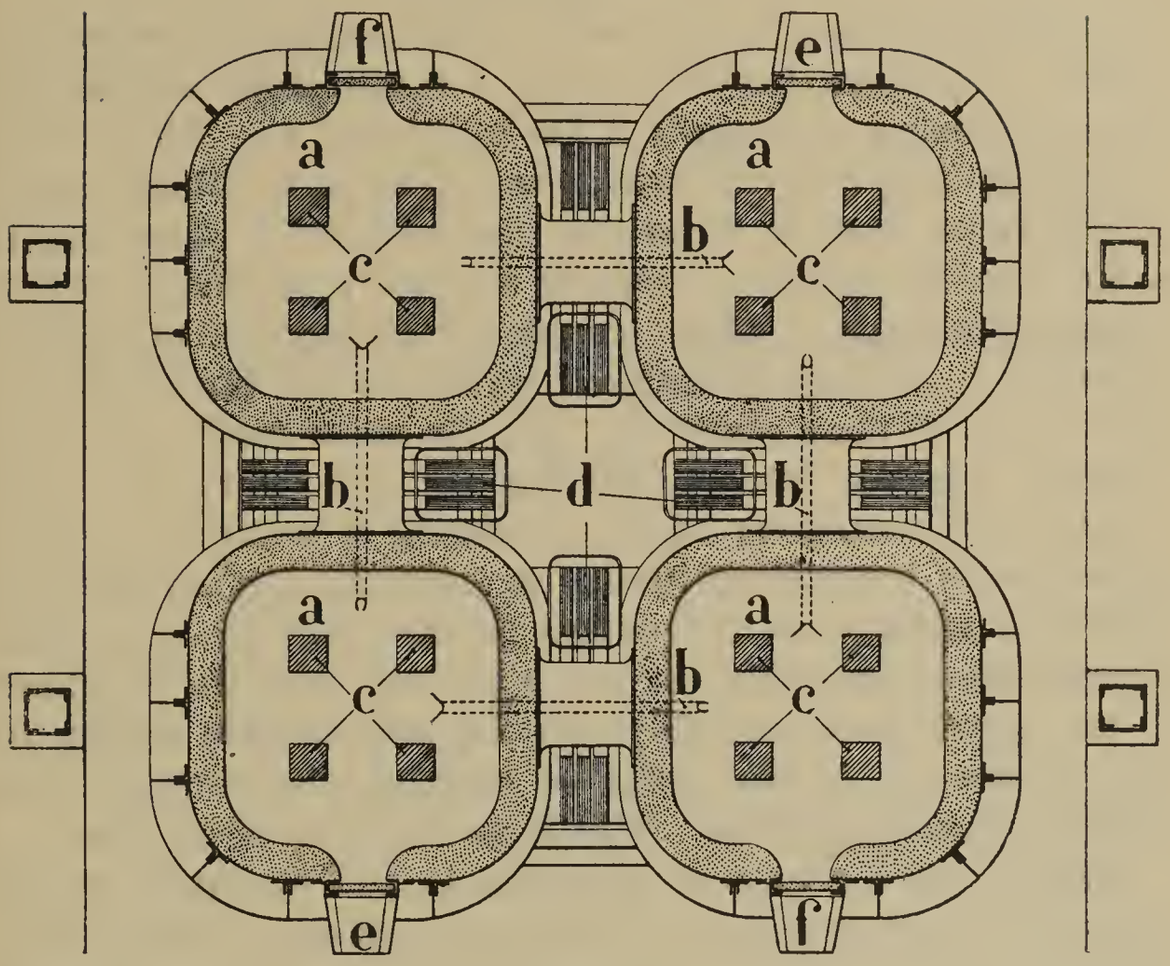


Fig. 14.

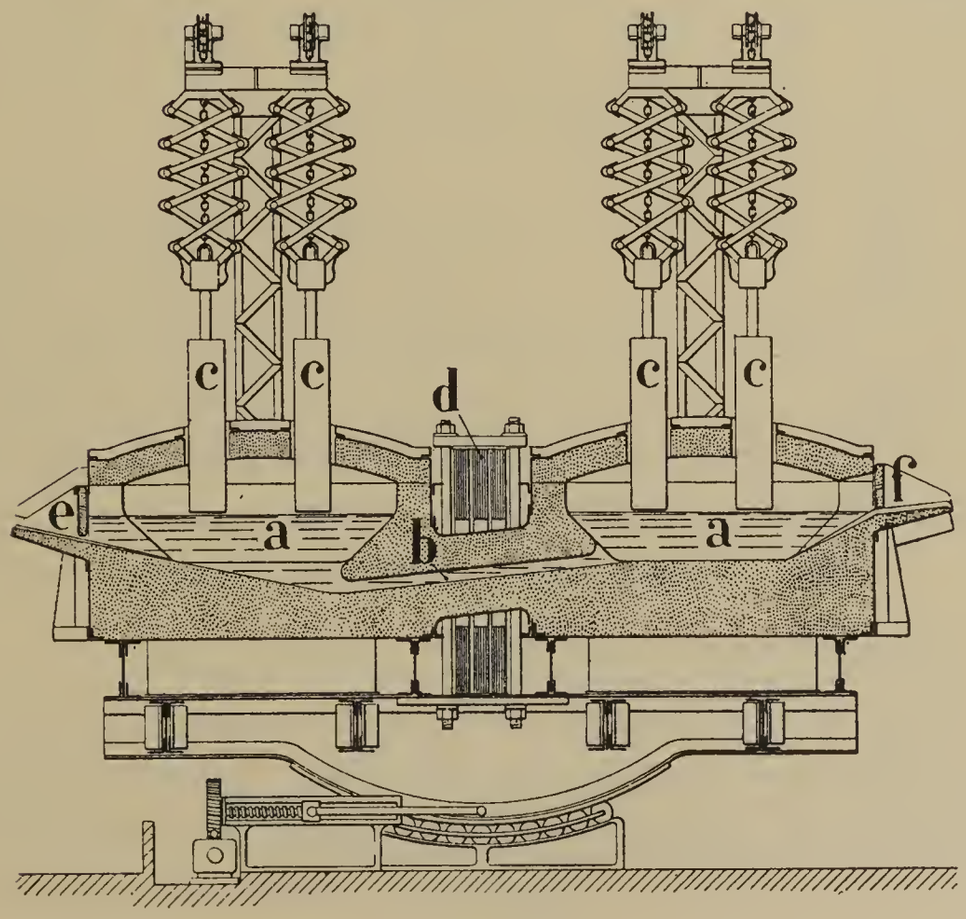


Fig. 15.

the principal heating current and of the supplementary heating current. A mixed furnace giving a much more satisfactory effect in practice is shown in Figs. 10, 11 and 12. These show diagrammatically two reservoirs, 1 and 2, united by tubular canals *a*, inclined in opposite directions. Around one of these canals is an induction system *c* carrying a primary winding *d* and a secondary winding *e*, whose terminals are connected to the two electrodes *b*, leading the induced current to the surface of the bath in one of these reservoirs. On the other hand, like in an ordinary induction furnace, one has the two reservoirs 1 and 2 with their connecting canals *a* forming a secondary circuit. There results the internal heating in the body of the metal and superficial heating at the surface in the reservoir (2). The electrodes being movable, one can, moreover, vary the resistance of the circuit and thus distribute the total electric energy in such manner as is convenient or desirable, between the two secondary heating systems. This is an important advantage.

One can place a pair of electrodes in one reservoir, or one electrode in each reservoir. The furnace shown in Figs. 13-15 has been designed for 6,000 kw., and to furnish 50 tons of metal per cast.

A paper presented at the Fifteenth General Meeting of the American Electrochemical Society, at Niagara Falls, Canada, May 6, 1909; President E. G. Acheson in the Chair.

CALCULATIONS OF A GIN SELF-CIRCULATING INDUCTION STEEL FURNACE.

By Gustave Gin.

(Translated by Jos. W. Richards and Carl Hering.)

In a paper read before this society in 1907[1] the writer presented the theoretical bases for the calculation of induction furnaces. In the present paper some practical applications of those calculations are given.

To show the possibilities of such furnaces for high powers using only normal frequencies, we have compared as examples two furnaces of 400 and 790 kw. The first is supplied by current at a frequency of 5 (Case I), the second at 25 (Case II). The first was the condition imposed at the Essen works of Krupp; the second will be the conditions at a factory we are about to erect at St. Marie de Cuines in the Savoie.

Data for the Construction.

	I.	II.
Power at terminals of primary in kw	420	790
Primary voltage adjustable from	3,500 to 4,000	500 to 550
Frequency in periods per second	5	25
Cross section of iron in transformer, in sq. cm., insulation not included	8,950	4,200
Maximum contemplated induction	9,000	9,000
Diameter of tubular channels in cm	17	12

The resistivity of the melted metal is assumed as varying between 140,000 and 200,000 electromagnetic units.

Calculations of the Two Transformers.

To determine the dimensions and constants of the two transformers we must first know some auxiliary variables, viz.: The resistance of the secondary, the reluctances, the phase lag of the

[1] Trans. Am. Electrochemical Society, **12**, 97 (1907).

transformer, the number of primary turns—values which follow from each other.

A. Calculations of the phase difference of the transformer.

This is given by the formula:

$$\tan \varphi = \frac{r_2 R}{4 \pi \omega} + \frac{4 \pi \omega}{r_2} \left(\frac{1}{R_1} + \frac{1}{R_2} \right) \qquad (1)$$

in which:

r_2 is the resistance of the secondary.

R is the reluctance corresponding to the resultant flux common to the secondary and to the two primary windings.

R_1 the reluctance corresponding to the two fluxes which traverse the primary windings without traversing the secondary.

R_2 the reluctance corresponding to the flux which traverses the secondary without traversing the primaries.

B. Calculation of the secondary resistance.

The single circuit constituting the secondary is composed of three channels of different sections, and its resistance is found from the formula:

$$r_2 = \rho \left(k_1 \frac{l_1}{s_1} + k_2 \frac{l_2}{s_2} + k_3 \frac{l_3}{s_3} \right) \qquad (2)$$

in which:

	I.	II.
ρ is the mean resistivity of the metal of the bath;		
l_1 developed length of the first reservoir in cm.....	160	200
l_2 developed length of the second reservoir in cm.....	120	200
s_1 mean section of the first reservoir in sq. cm.....	2,000	2,600
s_2 mean section of the second reservoir in sq. cm.....	1,480	2,600
l_3 total length of the tubes in cm.....	700	600
s_3 section of the tubes in sq. cm.....	227	113
k_1, k_2, k_3 are coefficients which concern the mean sections.		

Taking the formulas of Lord Kelvin for the apparent resistance of conductors for variable current the ratio $K = \frac{Rd}{Rc}$ is approximately unity when the expression $\sqrt{\frac{M \pi a^2 \omega}{\rho}}$ is between 0 and 0.5 (*a* being the radius of the conductor).

For limited values comprised between 0.5 and 1.5, the ratio k is given by the equation:

$$k = 1.077 - 0.312 \sqrt{\frac{M \pi a^2 \omega}{\rho}} + 0.315 \frac{M \pi a^2 \omega}{\rho}$$

From these formulas, for the mean value $\rho = 160{,}000$, it follows that:

	I.	II.
k_1	1.125	1.373
k_2	1.000	1.373
k_3	1.000	1.000

Inserting these values in (2) gives:

r_2	$3.22\,\rho$	$7.40\,\rho$

From these the following values of r_2 are deduced:

ρ	I.	II.
140,000	$r_2 = 451{,}000$	$r_2 = 1{,}035{,}000$
160,000	515,000	1,180,000
180,000	580,000	1,360,000
200,000	645,000	1,480,000

C. Calculation of the reluctances.

The form and contour of the magnetic circuit being given, one determines by a summary calculation the approximate section of the magnetic core, and thence deduces the dimensions indicated in the following sketch (Fig. 1):

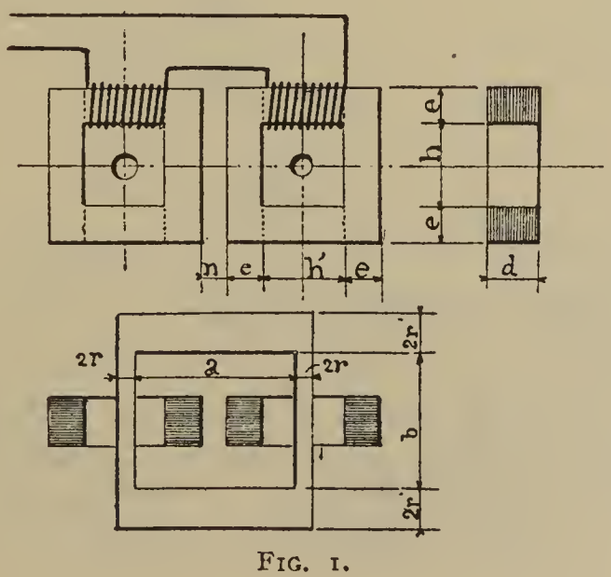


FIG. 1.

Calculation of R. The mean development of a core is the same in the two cases, hence

$$R = \frac{1}{2Ms}$$

in which

$$l = (167 + 186)\ 2 = 706 \text{ cm.}$$

s in sq. cm. = 4,475 (I) 2,100 (II)

Hence

$$R = \frac{0\,79}{M} \text{ (I)} \qquad \frac{1.68}{M} \text{ (II)} \qquad (4)$$

Since M can not be determined until B is known, we will return later to equation (4).

The calculation of R_1 is made by the formula

$$\frac{1}{R_1} = \frac{hd}{h^1} + \frac{2\,(d + h + 2e)}{\pi} \log. \frac{\pi e + h^1}{h^1} + \frac{h + 2e}{\pi} \log. \frac{\pi\,(e + n) + h^1}{\pi e + h^1} \qquad (5)$$

in which

		I.	II.
h	=	116	116
h^1	=	97	97
e	=	70	40
n	=	48	80
d	=	83	65
Whence $\frac{1}{R_1}$	=	387	265
and R_1	=	$2{,}580 \times 10^{-6}$	$3{,}775 \times 10^{-6}$

Calculations of R_2. In the formula:

$$R_2 = \frac{\pi}{a \log. \frac{2ab}{r^1 (a + \sqrt{a^2 + b^2})} + b \log. \frac{2ab}{\sqrt{rr^1}\,(b + \sqrt{a^2 + b^2})} + 2\sqrt{a^2 + b^2} - 2(a + b)} \qquad (6)$$

make:

		I.	II.
a	mean =	240	260
b	" =	228	210
r	" =	8.5	7·5
r^1	equivalent .	24	28.8

Whence:

R_2 (e.m.u.) =	$3{,}880 \times 10^{-6}$	$2{,}950 \times 10^{-6}$
$\frac{1}{R_2}$ =	251	335

D. Number of turns and voltage of primary.

We have:

$$n_1^2 = \frac{E_1^2}{W_2 \left[r_2 + \frac{16\,\pi^2\,\omega^2}{r_2} \left(\frac{1}{R_1} + \frac{1}{R_2} \right)^2 \right]} \qquad (7)$$

Calculating the number of turns necessary in the primaries of the two furnaces for the case in which the resistivity is a maximum, and using the maximum primary voltage, we have:

	I.	II.
r_2	645,000	1,480,000
E_1^2	4,000	550
W_2	420	750

Whence formula (7) gives:

	I.	II.
n_1	232 turns	13 turns

The voltage necessary to apply to the terminals of the primary in order to furnish in the secondary powers of 420 kw. and 750 kw. with the different resistivities concerned, is then calculated as follows. Formula (7) can be written:

$$E_1^2 = n_1^2\, W_2 \left[r_2 + \frac{16\,\pi^2\,\omega^2}{r_2} \left(\frac{1}{R_1} + \frac{1}{R_2} \right)^2 \right]$$

from which the following values are derived:

(in microhms) (cb. cm. units)	I. E_1	II. E_1
140	3,554	542
160	3,695	544
180	3,855	547
200	4,000	550

E. Calculation of section of core and the assumed induction.

We have assumed B = 9,000 for the value of the maximum induction. The formula

$$E_1 = \frac{n\ \omega\ \varphi\ 10^{-8}}{\sqrt{2}} \qquad (8)$$

gives the section of the iron which was assumed:

	I.	II.
s in sq. cm.	8,950	4,200

The different inductions resulting from the primary voltages are:

ρ	φ		B (max)		M	
	I	II	I	II	I	II
140	69.1×10^6	36.7×10^6	7,710	8,725	2,370	2,270
160	72.0×10^6	37.0×10^6	8,030	8,800	2,350	2,270
180	74.2×10^6	37.3×10^6	8,300	8,875	2,320	2,260
200	77.1×10^6	37.7×10^6	8,640	9,000	2,280	2,240

F. Return to calculation of R.

We may now calculate R from formula (4):

ρ	R I	R II
140	33.3×10^{-6}	74.0×10^{-6}
160	33.5×10^{-6}	74.0×10^{-6}
180	34.0×10^{-6}	74.5×10^{-6}
200	34.6×10^{-6}	75.0×10^{-6}

G. Power factor of the furnaces.

The formula (1) gives, for the two transformers:

$$\text{For frequency } 5,\ \tan\varphi = \frac{r_2 R}{395} + \frac{252,100}{r_2}$$

$$\text{“ “ } 25,\ \text{“ } = \frac{r_2 R}{1980} + \frac{1,188,000}{r_2}$$

ρ	tan φ		cos φ	
	I.	II.	I.	II.
140	0.5952	1.178	0.858	0.647
160	0.5317	1.044	0.882	0.671
180	0.4850	0.906	0.900	0.733
200	0.3595	0.846	0.9075	0.763

H. Efficiency of the transformers.

We will calculate this for an assumed resistivity of $\rho = 200$ microhms per cubic centimeter. The operating data are:

	I.	II.
W_2 kw.	400	750
N_1 turns	232	13
E_1 volts	4,000	550
B (max.) gausses	8,640	9,000
r_2 microhms-cm.	645	1,480
Cos. φ	0.907	0.763
I_1 amperes	117	1,920

Joule effect:

$$W_J = r_1 I_1^2$$

	I.	II.
Current density, amperes per sq. cm.	150	100
Cross-section copper conductors, sq. cm.	0.91	19.20
Length of copper conductors, cm.	171,680	5,460
W_j in watts calculated	3,930	1,600

Hystereses losses: These are given by the formula:

$$W_H = 10^7 \times f \times \eta \times V \times B^{1.6}\ (\text{max.})$$

in which:	I.	II.
V in cb. cm.	5,960,000	2,880,000
f	5	25
B (max.)	8,640	9,000
η	0.0022	0.0022
whence W_H in watts	12,000	30,300

Foucault current losses: These are given by the formula:

$$W_f = 5\ P \times f^2 \times B^2 \text{ max.} \times 10^{-12}$$

in which	I.	II.
P in kg.	46,500	23,240
whence		
W_f in watts	440	5,580
Total losses:		
In watts	18,340	37,480

The efficiencies are, therefore:

$$\frac{400{,}000}{418{,}340} = 0.955 \quad \text{(I)} \qquad \frac{750{,}000}{787{,}480} = 0.952 \quad \text{(II)}$$

DISCUSSION.

Mr. Carl Hering (*Communicated*): In this paper, Mr. Gin gives the resistivity of steel in electromagnetic units. Practicing engineers, however, generally prefer to use the more practical units, namely, the ohm, cb. cm. or cb. in. units of resistivity, and as the conversion of one to the other is troublesome in so far that errors are likely to be made, I have reduced his figures to practical units and have taken the opportunity to add others for the sake of comparison and for giving an idea of the numerical values of these constants.

In the table below, the resistivity units are in terms of the ohm. cb. cm. or the ohm, cb. in. units, and the conductivities in the reciprocal ohm (or mho), cb. cm. or cb. in. units. The reference numbers designate the origin of the data, which is given below the table. It will be noticed that the resistivities of

molten iron and steel are roughly about ten times that of the solid metal at ordinary temperatures; also that molten iron appears to have a resistivity of the order of, and approximately equal to, that of mercury at ordinary temperatures. It will also be noticed that more reliable information concerning these constants is badly needed, as this data is of great importance in the proper calculation of electric furnaces for steel and iron.

	Material	Temp. C°	Resistivity		Conductivity	
			Cb. Cm. Units	Cb. Inch Units	Cb. Cm. Units	Cb. Inch Units
1	Fused Steel . .	Not given.	0.000,140	0.000,055	7,140	18,100
2	Fused Steel . .	Not given.	0.000,200	0.000,079	5,000	12,700
3	Fused Cast Iron	1280 – 1340	0.000,16	0.000,063	6,250	15,900
4	Iron & Cast Steel	about 1300	0.000,114	0.000 045	8,750	22,200
5	Puddle Steel . .	15°	0.000,014,1	0.000,005,54	71,100	181,000
6	Bessemer Steel .	15°	0.000,023,2	0.000,009,16	43,000	109,000
7	Pure Copper . .	15°	0.000,001,687	0.000,000,664	592,800	1,505,000

1. Gin. From present paper; lowest value 140,000 electromagnetic units.

2. Gin. From present paper; highest value 200,000 electromagnetic units.

3. Gin. From his paper on "Note on the Electrical Resistivity of Iron and Steel at High Temperatures," Trans. Amer. Electrochem. Soc., Vol. VIII, 1905, p. 289. This I pointed out in the discussion was a million times too small; this correction has been made here.

4. W. Kohlrausch. Landolt & Boernstein, 2d ed., p. 468. The conductivity of cast steel at nearly white heat is given as 0.826 in terms of mercury at 0°, and that of electrolytic iron at yellow heat as 0.8196. Hence, approximately 0.823 for either is near enough for the present comparisons.

5 and 6. Kirchhoff & Hansemann. Both taken from the L. & B. tables, 3d edition, p. 716, in the form of the conductivity in centimeter units.

7. The Matthiessen value according to Lindeck, given here merely as a standard of comparison.

A paper read by Mr. F. A. Lidbury, at the Fifteenth General Meeting of the American Electrochemical Society, at Niagara Falls, Canada, May 6, 1909; President E. G. Acheson in the Chair.

DECARBURIZATION OF FERRO-ALLOYS.

By Gustave Gin.
(Translated by P. McN. Bennie.)

In some electrometallurgical works ferro-alloys of low carbon content are made by first reducing the mineral in the presence of a suitable quantity of carbon; then the accumulated slag is tapped off and there is placed upon the surface of the carburized metal a bath of ore which gradually oxidizes the carbon contained in the reduced metal.

It is generally admitted that such decarburizing requires a prolonged superheating, the length of which varies inversely with the carbon content desired.

It would seem to result from this practical observation that decarburization becomes more easy and complete with elevation of the temperature of the bath.

In our opinion the facts are altogether different.

In effect, the refining of a carburized alloy is produced not only by a superficial reaction between the metal and the fused slag in contact therewith, but also, and perhaps in larger measure, by an intermolecular reaction between the combined carbon and the oxide dissolved in the metal.

But all the metals of the iron family have the property of dissolving a certain proportion of their own oxide, and it is probable that the proportion of the oxide dissolved increases with the temperature. An elevation of the temperature of the bath to be decarburized increases, therefore, the proportion of the decarburizing agent needed; but it is not proved that it sensibly increases the immediate decarburizing action. In fact it seems that at high temperatures there exists a chemical equilibrium between the carbon and the dissolved oxide of which the reciprocal reaction should increase upon cooling and should reach

a maximum at a temperature slightly above the point of solidification of the metal.

It is well known that when fused carburized ferro-chrome is superheated in the presence of an oxidizing slag and the entire mass allowed to cool, it is regularly found that as it cools down, the surface of the previousiy tranquil bath becomes the seat of ebullition, at first slight, but increasing in intensity up to the moment immediately preceding solidification.

It is likely that this ebullition is caused by the disengagement of oxide of carbon, due to deoxidation of the dissolved oxide by the carbon present in the alloy.

It is naturally very difficult to account for these circumstances and the exact causes of the phenomenon, because in any of the observed cases neither the variations of heat of formation of the metallic carbide nor the oxide present are known; nor are the variations of the specific heats of the components and their products within the temperature ranges considered known exactly.

We feel, however, that this is an example of the principle advanced by Le Chatelier, that an increase of temperature favors endothermic (heat absorbing) reactions and a lowering of temperature exothermic (heat evolving) reactions.

A paper read by Mr. F. A. Lidbury, at the Fifteenth General Meeting of the American Electrochemical Society, at Niagara Falls, Canada, May 6, 1909; President E. G. Acheson in the Chair.

PREPARATION OF FERRO-VANADIUM BY ELECTROLYSIS.

By Gustave Gin.
(Translated by P. McN. Bennie.)

I have studied various means of producing vanadium electrolytically suggested by the principles already applied to the manufacture of aluminium. I have sought a solvent having a low fusing point, suitable fluidity, slight vapor tension and low electrical resistivity. As to the compound to be electrolyzed, it is naturally desirable to select the least exothermic one, but this latter condition is not always easily reconciled with the other conditions of the problem.

It is necessary furthermore that the compound electrolyzed should decompose without furnishing by-products which would alter the composition of the solvent, as this should serve indefinitely, in theory at least.

It is also necessary that the lining of the furnace should be infusible and but little attacked by the electrolytic bath.

Finally the cathode should not be of carbon, because the deposited metal would be carburized by contact with it.

I have selected vanadium trioxide as the compound to electrolyze, and calcium fluovanadate $V_2F_6.3CaF_2$ as the solvent.

The anodes are of carbon. The lining is of pure alumina fused in an electric furnace, agglomerated with tar and a little vanadic anhydride. This is heated to a bright red and there is then obtained a perfectly strong and compact mass.

The cathode is formed by coneshaped conductors of pulverized and agglomerated ferro-vanadium, which pass through the lining material and come out flush with its surface. At their lower parts these conductors are bedded in graphite resting upon a copper plate connected with the means for carrying current to the negative pole of the generator. The metal first deposits upon

the upper ends of the cathode cones, which become covered with a solid sheet, that continues to enlarge until they meet.

I have not been able to tap the metal, because the temperature necessary to do this is above that of the volatilization of the bath.

When a sufficient quantity of metal has been deposited the electrolytic bath is emptied and the metal allowed to cool. The bottom of the furnace is then removed and the plate of metal separated from the adhering cathode tips.

The current density most suitable at the anodes is 4.5 amperes per square inch of their section. (0.7 amperes per square centimeter.)

A paper read by Mr. F. A. Lidbury, at the Fifteenth General Meeting of the American Electrochemical Society, at Niagara Falls, Canada, May 6, 1909; President E. G. Acheson in the Chair.

NOTE UPON THE MANUFACTURE OF SILICO-VANADIUM.

By Gustave Gin.
(Translated by P. McN. Bennie.)

I have obtained the silicide SiV_2 by reducing in an electric furnace a mixture of vanadic acid, silica and coke in the proportions required by the equation:

$$3V_2O_5 + SiO_2 + 13C = 2V_2O_2 + SiV_2 + 13CO$$

This amounts to approximately 10 parts of vanadic acid, one part of silica, and one part of coke, by weight. This is accomplished with a current density of 1,290 watts per square inch (200 Watts per square centimeter) of cross section of the electrodes. A notable amount of the vanadic acid is volatilized. The volatilization is very much reduced by substituting vanadium trioxide, according to the equation:

$$3V_2O_3 + SiO_2 + 7C = 2V_2O_2 + SiV_2 + 7CO$$

By using commercial materials I have obtained a silicide having the following composition:

Vanadium	71.16	per cent.
Iron	5.40	" "
Silicon	22.16	" "
Carbon	0.72	" "

The manufacture of the double silicide of iron and vanadium is more easily accomplished than that of the vanadium silicate, by reducing vanadium trioxide by means of rich ferro-silicon.

The very brittle 60 per cent. ferro-silicon is powdered and mixed intimately with vanadium trioxide. This is agglomerated

with 4 to 6 per cent. of coal-tar pitch and moulded into briquettes or oval balls which are charged into a double-hearth furnace with a rammed magnesite bottom.

Reduction follows conforming to the formula:

$$4V_2O_3 + 4FeSi_2 + 4C = Fe_4\,Si_5V_6 + V_2O_2 + 3SiO_2 + 4CO.$$

I have obtained thus a silicide containing:

Vanadium	45.04	per cent.
Iron	33.52	" "
Silicon	19.40	" "
Carbon	0.62	" "

I have also obtained vanadium silicide, or the double silicide of iron and vanadium, by acting in the electric furnace upon vanadium tri-oxide or tetra-oxide with carborundum, or with a mixture of carborundum and rich ferro-silicon.

A paper presented at the Fifteenth General Meeting of the American Electrochemical Society, at Niagara Falls, Canada, May 6, 1909, President E. G. Acheson in the Chair.

THE PRESENT VALUE OF ELECTRICAL STRUCTURAL STEEL.

By Henry D. Hibbard.

Sometimes it happens that claims are made for a new thing of genuine merit so extravagant that when it falls short of fulfilling them all it meets trouble, opposition and delay in securing the recognition to which it is fairly entitled for the uses for which it is well adapted.

It is possible that the electric smelting of steel, now entering the commercial stage, is in danger of having its progress retarded by the zeal of its friends, who may claim more for it in some respects than the future will justify, and it therefore may be well to consider, from the standpoint of established steel metallurgy, what improvements may be reasonably expected from electric steel melting that will give it place in the face of competing processes, and what they are worth. However interesting it is from a scientific point of view, electric steel melting must prove profitable to those conducting it as a business or it will cease to interest a society like this, whose aims are in the field of applied science.

What follows is intended chiefly to compare the value of electric steel with that of steel made by the Bessemer and open hearth processes. Comparison with crucible steel is less needed because the differences are less.

The advantages which electric steel melting offers may in a general way be said to consist in the ability to melt or to retain melted a large quantity of steel in an environment either non-oxidizing or with access of oxygen to the metal under control, and also with controllable heat in the metal, both as to degree and duration. The beneficial result of these advantages lies more in the direction of improved qualities in the product than in lessening its cost.

As a result of these great determining factors the specific points resulting which tend to improve the product are the elimination of oxidation products, of the phosphorus and the sulphur, and, by the removal of these from the steel, to improve its quality and, when desired, to permit of less manganese being present in the finished metal. We will consider them in detail.

Oxidation products: These are the most uncertain of all the poisons to steel, because they are not determined and are dealt with by indirect methods. They may be itemized as being chiefly oxides of iron, manganese, silicon and carbon, and silicates of the two metals mentioned. Other oxides, silicates or gases are no doubt often present, but in very small quantities, except perhaps in the so-called alloy steels, but are not here considered.

The usual analysis does not reveal the presence or amount of these oxidation products. There is no method for the determination of oxygen suitable for regular work, and the usual determination of silicon gives no clue to its state in the metal, as to whether it is there as a silicide, silicic acid, or silicates, the latter two forms being those in which it is very harmful.

The electric furnace, by melting the stock in a non-oxidizing environment, either prevents the formation of such amounts of oxidation products as are usual in molten low-carbon iron produced by the pneumatic or open hearth processes, or, by keeping in a molten state such metal, however prepared, with some reducing element present, usually carbon or silicon, causes the elimination from it of such amounts as it may contain.

The actual benefit conferred on steel by the removal of the oxidation products cannot be set down in figures because of the lack of quantitative determinations of their amounts when present. On the usually determined physical properties they work harm, and they increase the susceptibility of the steel to corrosion. The great trouble they cause, however, comes in hot working the steel while it is still in the hands of the makers, from unsoundness in the ingot and redshortness, and also as surface blemishes of various kinds, such as checks, seams, un-uniform color, scale sticking irregularly and the like in the finished steel.

In rail steel ingots now being investigated at Watertown arsenal, polished sections show with a good magnifying glass

the presence of little shot of foreign matter, such as are more or less common in varying degrees in the ordinary grades of open hearth and Bessemer steel. These have been thought to consist of sulphide of manganese, but there is considerable evidence going to show that they consist, in large part at least, of the above mentioned oxidation products. They are rather small to collect for quantitative analysis, but their behavior with various reagents may yet determine their composition. There are two conceivable ways in which such shot may be present within the mass of the metal. One is that they are formed within the metal from the aggregation of oxidation products, and the other that they are mechanically mixed with the metal by violent mixing, especially that due to casting the steel, as oil and water may be mixed by such means if sufficiently rapid and prolonged. A third case is also possible, in which they are due in part to each of the causes given. The first case is probably the real one, but the fact cannot be considered proven as yet.

In the first case their composition will be that of the oxidation products plus, perhaps, some manganese sulphide, either intermixed or existing separately, though it may be in the same shot, and some manganese oxide, the manganese of these being a part of that in the final additions.

In the second case they will have the composition of the slag plus what oxides and sulphides they may have absorbed from the metal and final additions.

Assuming that these shot are due to the first mentioned cause, which apparently they must be at least in large part, the oxidation products which enter into them when first formed are practically dissolved in the metal, or at least are so finely disseminated as to be invisible. They do not collect into drops or shot until they are in a state of fusion, either because the heat has risen to their fusion temperature, or because that temperature has been lowered by fluxing with each other and with the oxide of manganese formed from the manganese in the final additions.

In the Watertown ingots examined, the metal within, where it had remained molten about fifteen minutes longer than at the surface, showed but a fraction as many shot per unit of area as the steel near the exterior. This indicates strongly

that time is very beneficial and indeed essential in removing such entrained particles.

Just what effect stirring has or would have on the steel before it solidifies is somewhat a matter of conjecture. It would seem that gentle stirring, by making the minute shot touch and amalgamate with each other, would help, for the larger shot so formed would be more effectively floated to the top by gravity. Violent stirring, on the other hand, might break up the shot into smaller ones, and so prevent their separation from the metal.

The electric furnace, then, in dealing with the oxidation products in crude steel enables the fusion to be continued at will until they are removed as completely as desired through agglomeration and gravitation, or by their reduction to elements through the action of some reducing element at the high temperature maintained.

Another matter, however, comes in here for consideration. If steel containing less of the oxidation products than is usual be found to have for that reason increased commercial value, something can be done when using the Bessemer and open hearth processes to attain some of that value, especially with the latter. In the Bessemer process the means to that end may perhaps be limited to variations in stock, blowing and final additions, followed by a limited and gentle stirring. In the open hearth process the time may be prolonged equally with the electric. Then by proper treatment of the slag and bath, and by allowing enough time, the oxidation products may be eliminated very largely—so much so as to approximate even electric steel in that respect.

If the electric steel furnace induces consumers to pay for high quality it will indeed have justified its existence. Until then its value because of its ability to eliminate oxidation products must be held as not determined.

Phosphorus: The basic open hearth can now produce regularly from very ordinary materials steel so free from phosphorus that very little is left for the electric furnace to do even if it were possible by its use to remove every atom. Given two steels substantially alike in other respects, but having respectively 0.01 and 0.02 per cent. of phosphorus, and he would be bold who would claim to be able to show a measurable difference in value for any purpose between them due to that fact. The

elimination of an additional hundredth of a per cent. seems to have more of a sentimental than a commercial value. Before the days of basic linings, phosphorus was the great enemy of the steel maker—an enemy who held every inch of ground without loss, and whose position seemed impregnable. Now, though pretty well cowed, it seems as if fear that it might in some way again be a menace to quality, leads us to attach undue importance to its absolute extinction.

The value then of the ability of the electric furnace to make structural steel exceedingly low in phosphorus cannot be great from a commercial point of view.

Sulphur: The effect of sulphur on the physical properties of the finished steel is so slight that satisfactory reasons do not appear for closely limiting and specifying its permissible content. As in the case of the oxidation products, the trouble from sulphur is more in evidence during manufacture than in the finished steel. The power of the electric furnace to eliminate sulphur from steel, while undeniable, must be held nevertheless as of little real value until the minimum attainable in the open hearth process is shown to have an important detrimental effect on the product.

Further claims may be made of other advantages and of certain beneficial effects akin to electrolytic action on the charge in the electric steel furnace, but be they well founded or not, it must be indubitably shown that the properties of the finished steel are better than those given by other methods at about the same or lower cost before the electric furnace can take its place as one of the standard commercial means for producing or finishing structural steel.

Conclusion.

It is stated that the German government is paying $4 a ton more for rails rolled from electric steel than for ordinary rails. Such action might be for either of two reasons: First, that the electric steel rails have been demonstrated to be worth that additional price; or, second, that the $4 amounts in part at least to a government subsidy aimed to put forward the development of the electric furnace. As the final test of value of a rail

consists in wearing it out by actual service, which can hardly have been done yet, it would seem fair to assume at this time that the $4 includes a subsidy. The total amount of such subsidy can not be very large up to date.

DISCUSSION.

PROF. J. W. RICHARDS: Mr. Chairman, it seems to me that the gist of Mr. Hibbard's paper is that electric steel must stand on its own feet in competition with other steel, and that no sentiment has any value in this commercial competition. This, I think, we all allow and agree to. But Mr. Hibbard leaves out of consideration the fact that 60 electric steel furnaces are now in profitable operation on exactly the basis which he sets for them.

MR. H. D. HIBBARD: The paper relates only to structural steel, and probably but a small fraction of the 60 furnaces mentioned by Prof. Richards are engaged in making such steels. In considering electric steel one must bear in mind the great difference in value of tool steels and steels used in building structures, track and machines. The former may bear costs absolutely prohibited commercially for the latter.

A general discussion at the Fifteenth General Meeting of the American Electrochemical Society, at Niagara Falls, Canada, May 6, 1909, President E. G. Acheson in the Chair.

THE ELECTROMETALLURGY OF IRON AND STEEL.

A GENERAL DISCUSSION.

MR. LOUIS SIMPSON: Mr. President and gentlemen, I have to congratulate you upon this convention. It would appear to me that the profession you represent is becoming very active. You have gone through a long period of experimentation, and I think I see before you a period of very great expansion. Although I am not by profession a chemist or metallurgist, yet in my little way I think I have been helping in their advance. Some nine years ago I became interested in a large water power in Canada, and in order to find work for that power, I studied the electric smelting of iron ores. I became interested in the good work done by our friend from Italy, Maj. Stassano, and I have to say this, that we owe the Major a very great deal. I believe that the work he did in Italy advanced the art of electric metallurgy in this country at least fifty years. I became quite satisfied in my own mind, as a business man, that under certain conditions which I knew existed in Canada, and which I also believe, and am sure, exist in the States, iron ore could be reduced, and from that iron ore the highest class of pig iron could be produced through the aid of the electric furnace. I was so satisfied of this that, as I could not get any capitalists to back up my opinion, because capitalists in Canada, like our friends in the States, were all doubting Thomases—but the evidences are accumulating upon every hand, proving that by means of the electric furnace iron and steel of a higher class than is now produced in the old fashioned furnaces can be produced—I say that I was so well satisfied on this point that at last I went to the then Minister of the Interior, Hon. Clifford Sifton, and placed before him the facts which I had accumulated. I placed before him the position of central Canada, where we had plenty of iron ore, not of a

quality suitable for the blast furnace, but otherwise excellent ore, but we had no coal; and I so interested the honorable Minister that he, at my request, recommended the appointment of a royal commission to proceed to Europe to investigate all the then known types of furnaces. I told the Minister I was satisfied that the principle underlying electric smelting was all right, but that I knew then of no furnace that was so constructed that iron ore could be commercially reduced. The Government of Canada, wise in their generation, appointed that commission, a commission which has now a reputation extending over the whole world —I mean the commission that was presided over by Dr. Haanei, whose address you heard this morning. That commission bore out the statements which I had made to the Minister, viz., that whilst it was quite possible to reduce iron ores experimentally, yet there was no furnace then in existence that would do it commercially, but they stated that the reduced metal could be refined and that good steel could be produced through the use of the electric furnaces then in operation. Although that report was published some five or six years ago, it is only lately that the United States Steel Co. has been convinced that that report was correct. The Germans have been convinced, the Englishman has been convinced—there are steel furnaces working now in Sheffield. Our Sheffield friends do not like to publish just what they are doing, but I have the information from a source which I can rely upon, and I can assure you that there is not one, nor two, nor three such furnaces in Sheffield, but a good many more. I understand that the Messrs. Krupp, of Essen, than whom there is no concern that manages its business on more scientific lines, have adopted the electric furnace for the refining of metal made into steel. Here in Canada, however, we were mostly interested in iron ore reduction, and after the first commission went to Europe a second commission was sent to Sault Ste. Marie, where experiments were made and where it was definitely proven that an ore whose sulphur content made its use unprofitable in the blast furnace could produce, through reduction in an electric furnace, a pig iron lower in sulphur than can be produced to-day in any blast furnace. It was also proven that nickel iron—iron containing 2 or 3 per cent. of nickel—could be produced. We have heard lately a good deal

about the requirements in the iron and steel trade in reference to improved steel rails, and we have it on Mr. Schwab's word that rails made from nickel steel are to be the rails of the future. I am of the opinion that no nickel steel can be economically produced unless electric furnaces are used. After the report of the second commission was published, having heard of the good work done by Dr. Haanel, a number of young engineers and metallurgists in Sweden, without any assistance from their government, have spent $100,000 in experimentation, and the result was the furnace which you see here behind you (Dr. Haanel's diagrams). I saw that myself working in Sweden during last December. I was honored by a special invitation from our friends in Sweden, recognizing the little work which I had done in inducing our government to interest Dr. Haanel in these matters; and I can assure you that during the time that I was there that furnace worked like a charm. I have had a great deal to do with all kinds of machinery, and I could wish no new machines to start better than I saw that furnace start.

Now, gentlemen, I think that it is time for the iron and steel trade of the States to wake up on this matter and to recognize things as they are. I do not say that the electric furnace is going to supplant the blast furnace, but I say this: That there exist in the United States, and there exist in Canada, certain locations where pig iron can be produced with the electric furnace equal or superior to anything now made in the States, and at a cost as low or lower than is the cost to-day at Pittsburgh. Now, I know that there are a great many here who are interested in the iron and steel trade, and I desire them to take it from me that the time is past when you may throw this subject on one side and doubt whether it can be done. The principles are all laid down, and I think now that the furnace is so perfected that it is a commercial possibility worthy of the attention of every good business man. In Norway during this summer there will be a new works constructed which will use furnaces similar to that shown here for reducing iron, also electric furnaces for refining that iron to make steel. During this year there will be a works built in India, and there are other works now on the tapis. I myself hope during this year to start a company which will use about 80,000 horse-power for the purpose of reducing

iron ores found in Canada; and when I have that plant going I shall be very glad indeed to give an invitation to the Society to visit Canada again and inspect the works. (Applause.)

Dr. J. A. Mathews: Mr. President, I have made a few notes with reference to electric furnaces as the subject appears to me from my study of it for a number of years, and also from some practical experience in connection with probably the first commercial electric furnace that was built in this country, a 5,000 e.h.p. furnace.

One could scarcely have studied seriously the developments of the last decade without coming to the conclusion that there are several methods now known by which steel can be successfully made in furnaces which are electrically heated, either by induction, resistance or arc, or by a combination of these methods. However dubious we may be about the commercial future of these methods, we can scarcely doubt the fact that steel, and very good steel, can be electrically made. As to just how good this steel is, compared with the product of the older methods, there may still be doubt in the minds of many. Perhaps the electrochemists or the inventors of the process may have claimed too much. In his presidential address before the Iron and Steel Institute a few years ago, Sir Robert Hadfield intimated that such might be the case when he stated that the trouble with the electrometallurgists was that they assume that all steel as now made is fundamentally wrong. This may be putting the case a little strong, but I do believe they have made statements that they have not taken the trouble to substantiate by actual experimental data. For instance, it is generally assumed or claimed for each electrical process that the superiority of its product depends upon the fact that the steel is melted in a neutral or reducing atmosphere and hence the product is better deoxidized and freer from dissolved gaseous impurities. While this sounds reasonable, and I believe is true in most cases, I have never seen any experimental proof or any determinations of the gaseous content of electric steel. As scientific men, I ask you whether it would not be a good idea to make an exhaustive investigation of this subject, and while we are about it, make it equally exhaustive in regard to the gaseous impurities of steels made by the old processes? Would not an authoritative investigation of the sub-

ject be of tremendous interest and might not its results be of inestimable practical importance? Surely the desultory investigations that have been made of this subject for years past have been far from satisfactory, and even the methods of determination of these elements are not above suspicion as to their accuracy. Moreover, the influence of the casting and subsequent heats has not been studied in its relation to the gaseous contents and mechanical properties. To my mind an isolated test or two of specimens of steel taken at random, said to be Bessemer, open hearth or crucible, is of no value whatever. The whole history of the process by which it was made must be recorded. Such an investigation cannot be undertaken lightly; it will take years to complete, its outcome will be problematical, but is it not high time that it were begun? I have been pondering this subject in my mind for years, and am trying to develop a plan to undertake it. It is such a stupendous task that it cannot be done at odd times or in a college laboratory. Several workers must give their undivided attention to it for years. Are we ready for it? Would this Society support me in the organization and direction of such a work? It ought to be undertaken under works conditions where the materials can be watched from the beginning. As manager of a works where three distinct processes are in use—the basic open hearth, the crucible and the electric—I feel it a solemn duty to undertake it.

But to return to electric steel: As regards quality, few who have studied the subject at first hand, or who have read the reports of the Canadian Commissioners, the investigations that have been published by a score of metallurgists and by the inventors of these interesting processes, can entertain reasonable doubts but that several electrical processes are capable of producing steel fully equal to that of the older processes. To be sure, there are still those who believe that good tool steel can only be made by various blends of Swedish irons; who claim that the results of melting hammered Swedish bars are much superior to those obtained by melting rolled bars of the same material; who talk wisely about "body" in tool steel, but who never define what "body" is. They remind one of the student who, when called upon to define space said: "I can't exactly define space, Professor, but I have it in my head." Now, while it is

true that there seems to be an intangible something about tool steels which is not revealed by the ordinary analysis, yet the weak point in this talk about "body" is that it seems invariably to be developed in an astonishing degree in the particular brand of steel which the spokesman is trying to sell you. To my mind "body" is more likely to represent the embodiment of the sum total of care used not only in the selection of raw materials, but also in the melting, cogging, rolling and annealing of the steel and in the selection of the right analysis for a given purpose. But in selling goods it is often advantageous to appeal to the mysterious, even though it may lead to what Professor Arnold calls one of those great scientific tragedies in which an elaborate hypothesis is slain by an inexorable fact.

My interest in electrical steel began with my interest in steel itself as a vocation. I have carefully followed the development of processes, and having been connected with the tool steel branch of the industry, my first choice of processes was that in which melting only was done—similar to crucible melting. I am free to confess that the processes involving purification of crude materials to produce a high quality product did not appeal to me. But upon second thought, since pig iron, the base of all steel, requires to be purified by some method or other before it is suitable for tool steel, why not use the basic furnace followed by the electrical treatment, or the electric process alone when power is cheap, to produce a pure product. Surely these refined methods ought to yield as good a product as those crudest of methods, the Lancashire furnace and the puddling process, as a source of raw material for tool steel. One cannot wax enthusiastic in contemplation of a pile of muck bars—the crudest of all crude materials in the steel industry. And yet, remelted in crucibles, they yield a product of great merit. The irregularity in composition of the product is objectionable, but this difficulty may be lessened by the use of Swedish bar iron, which is a reworked iron, much freer from entangled slag and more uniform in composition. In this country the use of Swedish iron is fast passing away; the crucible steel industry of this country, with very few exceptions, is a mere business—not an art, as abroad. In the writer's works we use a Swedish iron which costs more in the bar than the finished product of some crucible mills sells for.

We retain tenaciously the best traditions of English crucible steel practice and methods, but we are not standing still. We have the first commercial electric furnace, I believe, that was built in the Western Hemisphere. We are making steel in it, and good steel, too. To the best of my knowledge and belief it is chemically superior and physically and mechanically superior to most, and equal to any crucible steel made. I say this not boastingly, but as a scientific man addressing scientific men. Other electrical processes may produce as good steel, but I doubt whether the product of any gas or coke fuel furnace, no matter how choice the raw materials used, can more than equal it. I believe I am stating the case conservatively when I say that this product is as good as the best, and all laboratory and practical tests of the product to date seem to point to this conclusion. But, gentlemen, this was not always so. Some steel was made in our furnace in the early days that was not what it should have been. The electric furnace is a new thing—you must develop a practice with it as with other processes. It is not an automatic machine; we experienced trouble with it; it required care and study and practice. If one wishes to start a new open hearth plant, skilled men can easily be had; but if one starts an electric process, where will he look for experienced men? Unlike poets, they are not born, but made, and the making is not without expense, anxiety and some failures.

To one contemplating the installation of an electrical furnace, the choice of process depends upon many things—the material to be produced and the materials from which it is to be produced; the location; the source of power, whether bought or manufactured. If bought, can it be used direct in the phase and frequency as produced, or must static or rotary transformers be provided, and if the latter, is a standard or special type required? Is the power factor satisfactory? Is the furnace control satisfactory; the repairs to linings excessive or are electrodes likely to cause trouble? The cost of power per unit of product, either bought or made, these and many other factors enter into the consideration of electrical processes for various local requirements and conditions. However, assuming that these matters have had sufficient attention, that sufficient care has been given to the development of a good furnace practice, then, in my

opinion, there can be no doubt but that success will attend the experiment, whichever of several processes may be adopted, and that another decade will witness extraordinary advancement in the development of electric steel manufacture for tool, rail, structural steel for severe engineering requirements, castings and the manufacture of ferro-alloys.

It would appear that so far as types of furnaces and processes are concerned, that we were fairly well supplied; attention now must be devoted upon the part of inventors to improving the furnace design, the lining materials, the electrodes if used, the power factor and thermal efficiency and thermal control. The user must develop his own works practice just as in past generations our predecessors had to do when the Siemens producer, gas-fired crucible furnaces, graphite pots, acid Bessemer, acid Siemens Martin, and later the basic processes, were new things and were looked upon with suspicion by many a good metallurgist.

Mr. Paul Girod (*Communicated*): In contradiction to the general opinion, one cannot succeed in bringing, by means of the electric furnace, steel previously melted in Thomas or Martin furnaces to the point of quality of crucible steel. The reasons why are not yet well known, but my opinion is the following:

It is a general opinion that steels manufactured in the Thomas or the Martin furnace and refined in the electric furnace are of such a quality that they may be compared with the best crucible steels.

However, our personal experience and the facts we know about the working of the electric furnaces used for the refining of metal previously melted in the one or the other kind of above mentioned apparatus, put us in a position to affirm that two kinds of steel of exactly the same final composition, but manufactured in different ways, viz., the one manufactured in the above described manner, and the other manufactured exclusively in the electric furnace by starting from cold raw material having the same composition as the hot metal from the Thomas or Martin furnace, will not show the same qualities, namely, not the same resistance to shock; and with regard to tool steels, not the same hardness, nor the same tenacity and durability after hardening.

From our experiments and without presenting a formal explanation of this fact, we judge that the difference comes from the fact that in the Martin furnace, and so much the more in the Thomas converter, the steel takes up metallic oxides, oxide of carbon, nitrogen, hydrogen, etc. The faculty of solution of these elements and combinations of elements generally increases with the heat of the metal. Now, by charging into an electric furnace this hot metal saturated with these elements and combinations of elements, the temperature of the metal is still further increased, and thus the elimination of these gases and oxides becomes more difficult.

From our experiments, we consider that in order to produce the deoxidation and get rid of the gases of such a metal, the temperature must be lowered to 700° or 900° C. We have, in fact, remarked that a Thomas steel charged hot into an electric furnace gives results very inferior to that of a steel obtained by charging this very same Thomas steel in the cold state into an electric furnace and reheating it progressively up to the temperature of tapping.

Therefore, we consider that prospects based on this process of refining, in the electric furnace, of steel previously melted in the Martin or Thomas furnace, may meet much disappointment, and we consider that the charging of cold metal into an electric furnace, however more expensive it may appear, leads to results which liberally compensate the increase of cost resulting from the cold charge, whenever the price of a kw. hour is 3 to 4 centimes (0.6 to 1 cent), as it is the case in most metallurgical works. When the price of the current is of only 1 to 2 centimes per kw. hour (0.2 to 0.4 cent), the most economical process, in any case, is that of the cold charge, on the condition, however, that the furnace be suitable, *i. e.*, that its working be regular and that it be possible to make in this furnace all chemical operations of refining from the oxidation of the carbon, manganese, silicon, phosphorus, to the recarburization, addings of alloys and desulphurization.

We may say that we never would recommend the manufacture of fine tool steels, for instance, starting from melted Thomas or Martin steel charged liquid into the electric furnace.

Prof. J. W. Richards: Mr. Chairman, a statement was made

in the reading of Mr. Turnbull's paper, if I caught it right, that in the furnace having a bottom pole, that is, an electrode passing through the bottom of the furnace into the bath, there was always a source of trouble in the hearth. Was that the statement?

MR. FITZGERALD: Yes, that was the statement. It had reference to a furnace-hearth made in the particular way that Mr. Turnbull describes, that is, starting with a bottom pole through the hearth, allowing it to gradually melt down until it was partly replaced by melted metal. It also referred to the difficulty of making repairs.

PROF. RICHARDS: Taking that statement as it was made, that the bottom pole is a source of trouble in the hearth, I may say that I have seen Mr. Girod's furnace, which has a bottom pole, and was very much pleased to see the way in which it has stood hard work on a furnace which had been working for a year or more. Mr. Girod himself showed me the furnace out of action, and the bottom poles passing through the magnesite hearth were perfectly intact; there had been no leaking around them. The water cooling is only on the outer projecting part of the pole and not on the part which is embedded in the hearth. Mr. Girod said there had been no leaking around them, and no trouble with them whatever; and in a letter from Mr. Girod, some statements from which I read before, there is a statement bearing directly on that point. He says: "One might think that the bottom poles are in danger of wearing out, but that is an error. A 1.8-ton furnace in our works has run for a year without renewing the bottom electrodes. On stopping, for inspection only, we found that they were changed to a depth of about 10 centimeters, and below that were the original poles, intact." I think, therefore, that, as far as Mr. Girod's method of introducing those poles is concerned, we may conclude that they are a permanent feature of the furnace and give no trouble whatever.

MR. FITZGERALD: Can Prof. Richards give us any information as to repairing the lining? For example, one of those furnaces is tipped and completely emptied and an attempt is made to repair the lining by, say, throwing on magnesite or dolomite; is there any difficulty about getting the furnace started again, that is, in getting the current to pass through the bottom of the furnace?

PROF. RICHARDS: The inner end of these poles is flush with the

lower surface of the hearth. The outside projecting part below the hearth is water-cooled, in order to make good connections with it. The pole itself is about as thick as my arm. In the furnace which I saw out of action, the metal was about 10 centimeters from the inner surface of the hearth. In practice it probably melts that distance down into the hearth, but if, on tipping the furnace, enough metal is left in to fill those cavities, you have good connection with the metal bath to start with.

MR. FITZGERALD: I will explain more clearly what I mean. If the furnace has been running for some time, supposing the bottom is worn out in a hole in between the electrodes, what I would like to know is how it is repaired. I have seen the Héroult furnace repaired. The furnace is emptied and they shovel magnesite or dolomite on the surface, which is spread on the bottom, and then is ready to go right ahead again. Now, in repairing the Girod furnace, if the bottom was badly cut and you cover all this surface with magnesite, would there not be some difficulty in starting up, or does that point ever arise?

PROF. RICHARDS: I should say that that would be a very minor difficulty, that almost any steel maker would know how to overcome it. I should put some scrap steel in on top of the electrodes, or lay a piece of scrap iron over the top to protect it when I was shoveling in the mixture of magnesite and rosin.

MR. LANE: I have been told that some hold the opinion that manganese is an element that is to blame for rapid corrosion of steel as compared to wrought iron, and that in the electric furnace it is possible to make a non-manganese metal. I should like to know if any corrosion experiments have been tried with such metal made in electric furnaces.

MR. R. MOLDENKE: In the manufacture of tubes they take care to keep the manganese down just on that account.

MR. H. D. HIBBARD: Mr. Chairman, it is rather a late day to bring it up, but in these papers we have had there have been a number of physical tests given, and in most cases, I noticed, the dimensions of the test bar were not given. A report of a physical test without a knowledge of what the test bar is, is almost valueless, and I would suggest that, if possible, the writers of these papers supplement these tables with information as to the size, and particularly the length, the diameter, of the full

section of these test bars. It is rather a late day to bring this up. It has been brought up many times before, but it seems to be neglected persistently.

PROF RICHARDS: I would call attention to the fact that in Maj. Stassano's paper he gave the dimensions of the test bars that were used in his tests.

As regards the final additions or deoxidants used in manufacturing electric furnace steel, Mr. Girod has sent to the secretary the following communication, which he desires read in the general discussion upon electric steel:

MR. PAUL GIROD (*Communicated*): We do not employ aluminium alone as a final addition to our steels, but use instead alloys which give as the results of their oxidation (deoxidation of the bath) liquid slags composed of oxides and silicates of several metals. We use especially:

Ferro-mangano-silico-aluminium: Mn 20, Si 20, Al 12 per cent.
Silico-calcium-aluminium: Si 45 to 50, Ca 20 to 30, Al 6 to 10.
Silico-aluminium: Si 40 to 60, Al 20 to 30 per cent.

We make these alloys of various compositions for different purposes. We also make and use silico-manganese of various percentages. Likewise alloys of silicon, aluminium and magnesium, and of silicon, aluminium, magnesium and calcium, in various proportions.

When adding silicon to steel we prefer performing deoxidation by very rich silicon alloy, 50 to 95 per cent. silicon; but for making silicon steels we prefer to use ferro-silicon, with 25 to 40 per cent. silicon.

MR. A. VICTORIN (*In part communicated*): In reading the advance copy of Mr. Hibbard's paper, I noticed his reference to the commercial features of electric steels. I have been engaged for over a year now in investigating the commercial merits of certain electric steel furnaces, and am prepared to furnish some data in regard to the value of commercially produced electric steels.

Admitting that the present state of the art is not favorable for the use of the electric steel furnace in the production of grades of material used in the manufacture of rails, structural steel, sheet steel, plates, etc., at present prevailing prices, it is evident that steels of higher grades physically, chemically and mechani-

cally, can be produced to-day uniformly and safely at a higher rate of profit in the electric furnace than by any other method in vogue.

A commercial proposition in the form of a graphical illustration will readily demonstrate this. I assume for this purpose a steel casting plant located within the industrial district of Philadelphia.

The plant is supposed to be equipped for the annual production of 12,000 tons of (principally machinery) steel castings, and is assumed to operate at full capacity.

This output was selected because it represents an attractive and reasonable commercial proposition, and also because it represents the maximum annual capacity of one (1) 5-ton electric furnace with hot charge (mixed process), or of three (3) 5-ton or two (2) 8-ton electric furnaces with cold charge (electric process).

The results shown relate to finished products, *i. e.,* salable steel castings.

The table includes the open hearth process (columns 1 to 7), the small Bessemer process (columns 8 to 14) and the electric furnace process (columns 15 to 19). The first two are subdivided into the non-electric (or ordinary) process and the mixed process. In the latter the electric furnace is charged with liquid metal from an open hearth furnace or a Bessemer converter.

Costs are given for various fuels as follows:

Natural gas, at 5 cents per 1,000 cubic feet;

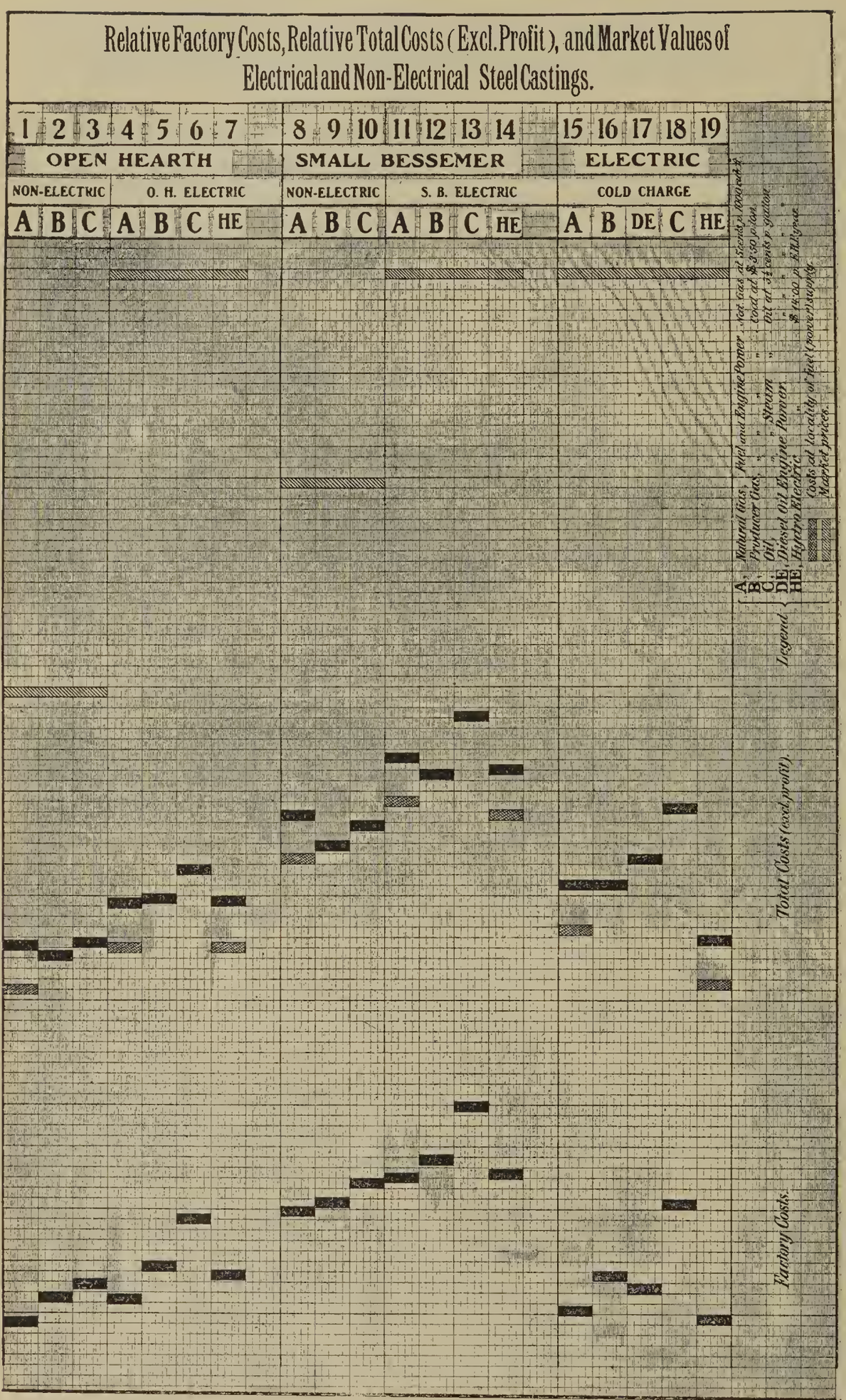
Producer gas, with coal at $3.50 per ton; and

Oil fuel, at 3½ cents per gallon.

With producer gas and natural gas the gas engine is used for power; with oil fuel the steam engine and the Diesel oil engine.

Rates for natural gas and hydro-electric power have reference to West Virginia and Niagara Falls respectively; they represent the lowest cost for fuel and power obtainable in these parts of the United States. Production and total costs are given for these localities and also (by adding freight charges) for Philadelphia.

The lower range of graphical data gives the relative factory costs of steel castings per ton; the upper range gives the relative total costs (exclusive profit).


Relative Factory Costs, Relative Total Costs (Excl. Profit), and Market Values of Electrical and Non-Electrical Steel Castings.
1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19
OPEN HEARTH
SMALL BESSEMER
ELECTRIC
NON-ELECTRIC
O. H. ELECTRIC
NON-ELECTRIC
S. B. ELECTRIC
COLD CHARGE
A B C A B C HE A B C A B C HE A B DE C HE
Legend
A. Natural Gas, Fuel and Engine Power - Net Cost at Steels 1,000 cub. ft.
B. Producer Gas, " " - Coal at $3.50 per ton.
C. Oil, " " - Steam " " Oil at 3½ cents per gallon.
DE. Diesel Oil Engine Power " " " " "
HE. Hydro Electric " " $14.00 per H.P. year
Costs at Locality of Steel Foundry
Market prices.
Total Costs (excl. profit).
Factory Costs.

The factory cost comprises all materials, the productive and non-productive labor cost and the cost of power and of repairs.

The total cost comprises the factory cost, the administrative and selling expenses, a factory profit of 10 per centum on the three items just quoted and the fixed charges.

The fixed charges represent 20 per centum of the total cost of the plant plus the working capital necessary to cover a period of six months.

The (vertical) distances between factory costs and total costs show the actual relative difference between these values. The absolute and relative cost values of electric steel castings (columns 14 to 19) when compared with those of the other processes demonstrate that the production *now* of electric steel castings is justified from a commercial standpoint. The chemical, physical and machining qualities of such castings, as well as the facility and safety with which any desired quality may be produced uniformly, place electric steel castings in the front rank in respect to commercial value and profit.

I have shown in the diagram also relative market values of the steel castings produced by the various methods, the assumption being that electric steel castings sell two cents higher per pound than those made by the small Bessemer process and four cents higher than open hearth steel castings.

The (vertical) distances between these market values and the corresponding total costs denote the commercial superiority of the electric steel castings, although the relative market value assigned to the latter is rather conservative.

Concluding I may mention that the rate quoted for hydro-electric power at Niagara Falls does not seem to favor the choice of that locality particularly for the manufacture of electric steel castings; more favorable inducements are desirable in regard to peak-loads.

To qualify somewhat more the illustration, which I presented at the recent meeting at Niagara Falls, in regard to the commercial status of electric steel castings, I desire to say that the costs of electric steel castings given by me are not based on the use of *cheap scrap,* which is frequently given importance in pointing out the advantages of the electric steel furnace process, but

on the use of a suitable and regular commercial scrap material, as is commonly practiced.

The cost of power is largely influenced by the operating arrangements of the foundry, especially under restricted production.

In the example cited by me (working at full capacity) the load factor for electric furnace operations is 67 per centum, in using hot charges, and 82 percentum with cold charges. The load factors are reduced, however, through the influence of the necessary operating system to 50 and 75 per centum respectively.

The influence of power cost is frequently misunderstood. This item, for the electric furnaces referred to, represents only 2½ to 3½ per centum of the entire production cost, using hot charges, and from 4 to 7 per centum with cold charges.

A similar misconception exists often in regard to the labor cost of *steel in the ladle,* which amounts to less than 3 per centum of the entire production cost.

The earnings, or profits, of the steel foundry examples, illustrated by me, depend naturally on the production factor. The open hearth process and the small Bessemer process will show losses when the production factor falls below 40 per centum, while electric process losses do not appear until production is reduced below 30 per centum (or even less), under the conditions quoted.

My statements are not made to infer that the electric steel furnace can be operated advantageously under any conditions. I believe, to the contrary that the advantages of an electric furnace installation must be manifest *before* active steps are taken.

Those fully familiar with the facts governing commercial production conditions will appreciate this expression.

Mr. Moldenke: I came here particularly to-day as representing the American Foundrymen's Association, of which I am secretary. I wished to learn something on the probable future of the electric furnace for the steel casting foundry. I desire to report to my foundry colleagues at the Cincinnati Convention next week, and as far as I have learned of your progress, I would form the following conclusions:

That you are not ready to make steel castings directly from the ore at a price low enough to justify the steel founder to look

into it as an investment. That you can, however, take steel scrap and even billets, and remelt as well as purify and cast into small castings and complete commercially with other processes. That you could do this even better, if you would use the ordinary methods of the regenerative furnace for the heating up to the melting point, and then apply the current for the final melting and purification. Where the method thus suggested would be applied in a works having molten steel, as for instance the large Bessemer or open hearth establishments, the problem becomes even simpler.

The high cost of the installation, and the large amount of power required will make it difficult for a foundry to consider the electric process. If, however, especially for the small castings industry, a very small installation is arranged for, and the actual melting by the current is put for the night shift, or when practically no other work is done in the shop, the initial expense for power installation will become greatly reduced.

As we have some 6,400 foundries in North America, and very many of these are looking seriously into the production of small steel castings, I would recommend that your members take up the matter seriously and in such a way that with a minimum of first cost and disturbance in an existing establishment, a small electric plant can be installed and operated, using only steel scrap and billets, preferable pre-heated by means other than the electric—say the soaking pit, or regeneration of gas and air.

(*Communicated*): I have presented a synopsis of the great electric steel meeting at Niagara Falls before the American Foundrymen's Association, in convention at Cincinnati, and can report the greatest interest taken in the matter. One of the sessions was wholly given over to the discussion of the small steel casting as made in the open hearth, the Bessemer converter, and in combination of each of these with the electric furnace (Paper by Dr. Bradley Stoughton). The foundryman is without question very much alive to the commercial possibilities of the electric process, and it would seem to rest with our electrometallurgical friends to make propositions that will cover the requirements and be commercially possible.

Mr. H. M. Lane: I have had a great many inquiries from foundrymen throughout the country as to how they could make

their own steel castings to fill a wide variety of specifications, and in many cases the expense was almost a negligible quantity. The proposition was to be able to get delivery and to get quality. Those two elements were demanded, and a tonnage, in some cases, not to exceed 1,000 pounds. In many cases they want to make a comparatively short campaign in each one. If some process can be developed which will enable a manufacturing concern itself to make its own steel castings to fit in with its equipment, that is, fit the equipment it is manufacturing, as it wants them, there will be a demand for them. If the process will utilize waste material about the plant, that is, iron borings, steel borings and such material as that, so much the better, and every plant has quantities of that kind of material. It has seemed to me for a long time that the electric furnace was a solution of the problem. I have had to recommend the introduction of small units in converter process, in crucible steel and in open hearth, in the last few years, where I know that they are having lots of trouble with it, and yet it is the only thing that is available to-day, and I do believe that if the electric furnace men would study that field and study also the composition of the alloys that are required for that work, that is, the composition of the steels and the material available in a plant, that they will find there a big field.

A paper presented at the Fifteenth General Meeting of the American Electrochemical Society, at Niagara Falls, Canada, May 6, 1909; President E. G. Acheson in the Chair.

THE WORKING LIMIT IN ELECTRICAL FURNACES DUE TO THE "PINCH" PHENOMENON.

By Carl Hering.

Two years ago the writer read a paper[1] before this Society on a new phenomenon he had noticed in an electrical furnace, which gives rise to serious troubles and which fixes a very positive limit beyond which the current and, therefore, the temperature in a certain class of electrical furnaces, cannot be increased; this phenomenon must, therefore, be reckoned with in that class of electrical resistance furnaces in which the resistor is a fluid, and the current density is high. For want of a better name at the time, the writer called it the "pinch" phenomenon, because this expresses its characteristic feature in a single word; as it has since then become generally known by this popular term both here and abroad, and is referred to in the literature on furnaces, it may be inadvisable to change its name now to a more dignified one.

Since the reading of that paper, inquiries have been received by the writer asking whether there was danger of encountering this very troublesome phenomenon in certain prospective furnaces; also what the laws concerning it are, and how this limit can be predetermined, if possible, when a furnace is being designed. The very serious consequences which may arise from this phenomenon and the very decided limit which it places on the current density or temperature, make it very desirable to know more about the liability of its occurrence and about the laws governing it. The purpose of the present paper is to analyze the phenomenon and to give its laws, as far as possible, from the scant amount of information existing about it.

The phenomenon is briefly as follows: When an electric

[1] "A Practical Limitation of Resistance Furnaces; the 'Pinch' Phenomenon." Trans. Am. Electrochemical Soc. Vol. XI, 1907, p. 329.

current, either direct or alternating, passes through a liquid conductor, that conductor tends to contract in cross-section, due to electromagnetic forces. This contracting force is small for relatively low current densities, but is quite large when they become greater, large enough to contract it to zero, that is, to rupture the circuit. This contraction is apt to form locally at some particular spot; it acts like the tearing of a rope at its weakest part; it forms a depression in the channel of molten material; it has the appearance of the liquid being pinched by an invisible force. Into this depression the floating, solid, infusible materials are apt to fall, thereby tending to prevent a reunion of the liquid and a consequent freezing of the charge before the obstacle can be removed. As it may become very difficult in such a case to start the current again, the result generally is that the furnace must be taken apart and rebuilt.

In order to make an analysis of the forces and conditions involved in this pinching effect, it is necessary first to examine its nature, its causes, and the actions which take place.

Dr. E. F. Northrup has shown in a very interesting and instructive paper[2] that this contracting force may be explained as due to the mutual attraction of the current elements in the conductor, just as parallel and like currents in different conductors attract each other. The present writer has shown since then[3] that this attracting force acts on the material itself which carries the current, as distinguished from merely acting on the current elements themselves, which would then tend merely to concentrate the current toward the center of the conductor; that is, it is the material and not the current which is forced toward the center by this attraction.

Dr. Northrup, in this same paper, has developed the mathematical relations for a conductor when its cross-section is circular, which enable one to calculate the forces without requiring any empirical constants. It may be of interest to add here that he has since designed and constructed a very interesting and promising current-measuring instrument based on this "pinch"

[2] "Some Newly Observed Manifestations of Forces in the Interior of an Electric Conductor." Physical Review, Vol. XXIV No. 6, June, 1907, p. 474.

[3] "An Imperfection in the Usual Statement of the Fundamental Law of Electromagnetic Induction." Proc. Amer. Inst. Elec. Eng. March, 1908, p. 339.

phenomenon, the deflections of which correspond very satisfactorily with those calculated by means of his formulas, thus confirming their correctness.

One of his formulas, which will be used below, is readily reduced to the following form, but it should be noted that it is rigidly correct only for conductors of circular cross-section:

$$P = \frac{C^2}{44{,}479{,}100 \cdot S}$$

in which P is the pressure in pounds per square centimeter at the center, acting axially, C is the current in amperes, and S is the cross-section in square centimeters.

The effect of the force which tends to contract the conductor is to squeeze the liquid out axially at the centers of the two ends. In his paper he describes how in this way a current may be made to produce a small fountain of mercury at the center of a vertical conductor of mercury.

In a furnace, the action of this "pinch" effect, therefore, seems to be that the liquid is forced along the horizontal central axis towards the ends, causing the level of the middle portion to diminish, while that of the ends rises; the liquid then flows back by gravity from the high to the lower parts, about as is shown in Fig. 1, which is a vertical section of the channel, the current flowing horizontally, parallel to the drawing. The liquid is thereby violently agitated (incidentally, it thereby also becomes well mixed), and from the top it appears as though a hole had broken out in the bottom of the furnace, into which the material was flowing rapidly, with the exception, however, that the average level does not diminish; the first appearance of the phenomenon was, therefore, a very strange and deceiving one.

An approximate mechanical analogy may be imagined, as shown in Fig. 2. Let a narrow channel of liquid be provided with two pipes at the bottom, as shown, each containing a force pump, say a propeller wheel, p and p, which sucks the liquid from near the center and forces it out near the ends, as shown by arrows. It will be seen that the effect will be a lowering of the level in the middle, the depth of the apparent contraction

increasing with the speed of the pumps. For a moderate speed an equilibrium will be reached, as at *a*, for instance, when the return flow is equal to that through the pumps. But at very great pumping speeds it is imaginable that the liquid could be sucked away faster than it could flow back, and, therefore, it would part at the bottom, as shown at *cc*. It will furthermore be seen that there may be a critical level, as *b*, for instance, at a little below which the inflow from the sides would be less rapid than the outflow through the pipes; it will then be unstable, for, if the inflow is interfered with for a moment, the level will fall until the liquid parts, as shown at *cc*. Hence, there is both a stable and an unstable level. It will also be seen that the viscosity of the liquid plays an important part, for with a thick syrup, for instance, the unstable level would be reached far earlier than with a very thin non-viscous liquid like gasoline.

Fig. 1

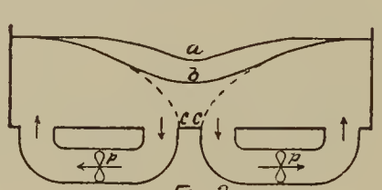


Fig. 2

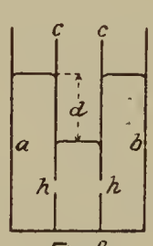


Fig. 3

This analogy, however, lacks one of the important properties of the electric phenomenon, namely, that the original contraction increases the current density in the contracted part (assuming the current to remain constant), and as the force increases with an increase of current density, as shown in the Northrup formula, this contraction will tend in turn to still further increase the force which is producing it, thereby further diminishing the cross-section. In the electric phenomena, therefore, the unstable state, that is, the state in which, for a constant current, the level will continue to fall until the break finally occurs, is apt to be reached earlier.

There is another and very important property of the electric phenomenon not possessed by the mechanical analogy. Suppose a certain relatively small current produced a stable level at *a*,

Fig. 2 (assuming this figure now to represent the electrical action), so that if disturbed a little, the same level would be restored. If now the liquid be mechanically depressed at that point by some external force, say by a piece of insulating material forced into it, or by the weight of heavy floating fragments which do not conduct, it will be seen that such a contraction of cross-section might thereby occur, that the increase in the current density is sufficient to produce the unstable state, resulting in a rupture, even though the current has remained the same. In other words, in the electric furnace an additional and purely mechanical force which produces a contraction of the cross-section tends to bring about the fatal rupture, even though the current alone would not have done so and might be well within the safe limit. Hence, the surface should be kept as clear as possible of heavy floating non-conducting particles. For similar reasons the "pinch" is always more likely to occur in that part of a channel where there is a partial constriction due, say to frozen slag, a slightly projecting brick, etc.

It will be seen from the above that the phenomenon is not of a simple nature, and that a purely mathematical solution cannot be depended upon absolutely for calculating actual cases, because such unknown and uncertain quantities as the viscosity, the frictional resistance of a liquid moving at high velocity in a liquid, the changes of density of the liquids at high temperature, etc., are involved; also because in actual practice irregularities are likely to occur which may upset all of the calculations. To develop a general and exact formula for rectangular sections, like the one above for circular ones, would be a troublesome task, and it would probably not be very simple to use. The writer will, therefore, limit himself in the present paper to a general analysis of the action, with such conclusions as can be deduced from it, and to developing some approximate formulas for the more usual cases occurring in practice.

Suppose an imaginary tank to be constructed as shown in Fig. 3, separated by conducting partitions, *c* and *c*, into three parts, each containing mercury; *hh* are small holes in these partitions half way down from the lower level. The middle part is narrower than the outer ones in a direction perpendicular to

the drawing. If now a sufficiently strong current be passed through it lengthwise, from *a* to *b*, the "pinch" effect will tend to contract the middle portion because its cross-section is less and the current density, therefore, greater. This will cause the mercury in it to be forced through the holes *hh* into the outer compartments, lowering the level in the central one until the difference in hydrostatic pressure, due to the difference in level *d*, is just balanced by the pressure of the "pinch" effect at the holes *hh*. In this way the latter pressure might be measured if the holes are at the center of the middle part; but the main

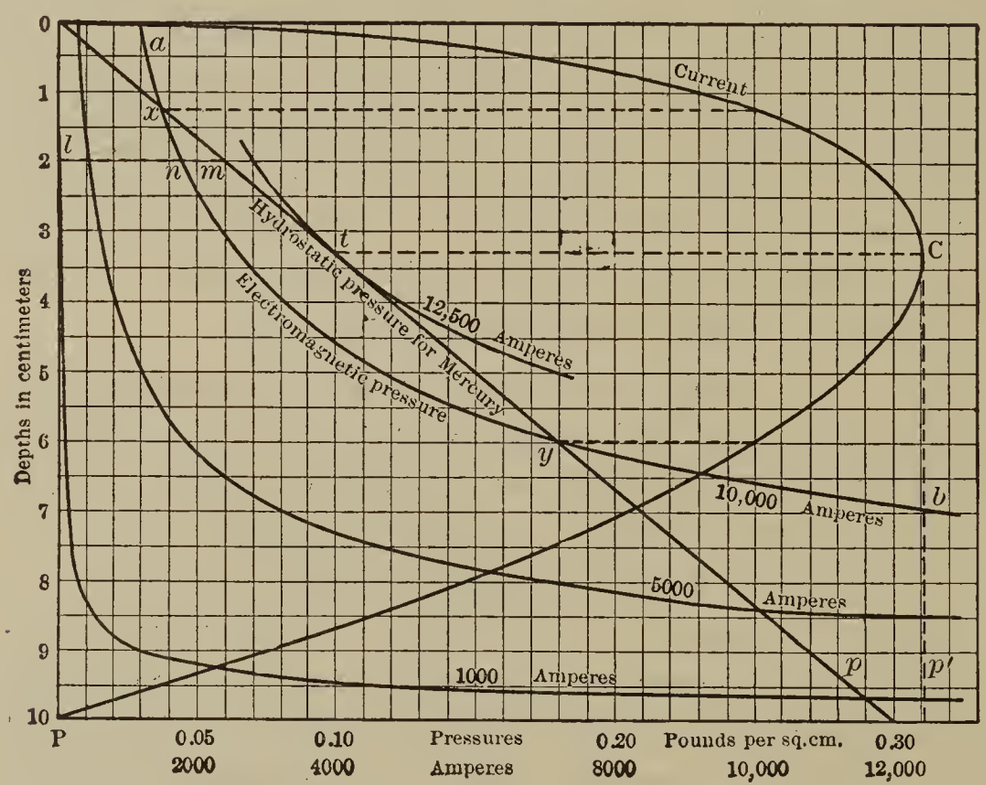


FIG 4.

point which this figure is intended to show is that the equilibrium will be reached when the electromagnetic pressure at the center of the contracted part is equal and opposite to the hydrostatic pressure due to the difference of levels.

This hydrostatic pressure is easily calculated for any given depth of the "pinch," and the Northrup formula gives the pressure due to the "pinch" effect, provided the cross-section of the contracted portion is always circular. This latter condition cannot be realized in practice with an open horizontal channel, but for the purpose of finding out the general nature of the

quantitative laws of this phenomenon, as distinguished from the specific values for the usual rectangular sections, it will not be improper to imagine this to be possible.

In Fig. 4, let the vertical distances *d* represent the differences in levels in centimeters for an original depth of 10 cm. of liquid, and the horizontal ones represent pressures in pounds per sq. cm.; let the liquid be mercury.

The hydrostatic pressure will evidently increase in direct proportion to the depth and will, therefore, be represented by a straight line *Op,* which is quantitatively correct for mercury. The "pinch" pressures are evidently independent of the specific gravity of the liquid, being dependent only on the current and the cross-section. Calculating these for the various differences of levels by means of the Northrup formula given above, for the centers of the contracted parts, gives for a current of, say 10,000 amperes, the curve *ab.* This curve merely gives the pressures which that particular current would produce if the column had contracted (from any cause whatsoever) to those differences of level, or had those respective cross-sections originally.

As was shown above, the equilibrium will be reached when these two opposing pressures balance each other; that is, when they are equal, which will be the case at the intersections of this curve with the slanting straight line. It will be seen that there are two such points, *x* and *y,* hence there are two different levels for the same current.

For the higher level *x,* which in this particular case means a depression of 1.2 cm. it will be noticed that if the level is lowered slightly by depressing it mechanically, say down to 2 cm., the hydrostatic pressure *lm* will be greater than the "pinch" pressure *ln,* hence the former will act to restore the liquid to its former level of 1.2. In other words, if disturbed, it will return to its level and hence the equilibrium is a stable one.

For the lower level *y,* however, which in this case represents a depression of 6 cm., the conditions are different. If in that case the level is disturbed, say by lowering it mechanically, it will be seen that now it is the pressure of the "pinch" effect (that is, the distance to the curve *ab*), which is the greater of the two, and this will, therefore, be the one which will act; but its

action is to diminish the cross-section still more, which means that this point is one of unstable equilibrium, the contracted section rapidly becoming smaller and smaller until complete rupture occurs.

It will be seen, therefore, that the current may be well within the safe limit, causing only the upper, small, and perfectly stable level, yet if some mechanical force then acts to depress the level to a lower point, the unstable level may be reached in which case the same apparently safe current will be sufficient to cause the rupture. Such a mechanical depression could be produced by some floating infusible material, a loose fragment of fire brick, etc., or by stirring with an insulated rod in a narrow channel. It is, therefore, not always safe to conclude that if the normal current produces only a slight depression, there is no danger of rupture.

By drawing the corresponding curves for 5,000 and 1,000 amperes, it will be seen that these two points of intersection move further apart as the current diminishes, which means that a disturbance of the level becomes less dangerous. On the other hand, the curve for the greatest possible current of about 12,500 amperes, becomes tangent to the straight line at *t*, which means that the two points have come together.

By calculating the currents required to reduce the levels to the various depths *d*, the curve *OCP* is obtained, the horizontal distances of which are currents instead of pressures. The curve is seen to be re-entrant, returning back to zero. Starting at *O*, where there is no depression, it will be seen that the current must be increased to large values before any marked contraction occurs. After that, however, the level falls quite rapidly with a small increase of current, until the maximum possible current is reached at *C*, after which even a smaller current will again be sufficient to balance the increasing hydrostatic pressure, because the cross-sections are less and the current densities are greater. The lower part of the curve is, however, only of theoretical interest, for at the maximum point *C* the state of unstable equilibrium begins, and in practice rupture, therefore, immediately follows; hence this lower half of the curve in practice becomes a vertical line *Cp'*.

If a horizontal line is drawn from the upper point of intersection x of the pressure curve for 10,000 amperes, to the current curve, it will be found to intersect it at 10,000 amperes, as it should. The same is true of the lower intersection or of any of the others; and the pressure curve for the maximum current of about 12,500 amperes, will be tangent to the straight line at t, namely at the same level as the maximum point, C, which important point will hereafter be termed the *critical point.*

For materials of different densities, the hydrostatic pressure is of course proportional to the density; but from the formula the current is proportional to the square root of the central pressure and therefore to the square root of the density; hence the currents for the critical point will not vary as rapidly as the densities of different materials. For instance, the density of molten iron, 6.88, is just about half that of mercury, but the values of the current curve will be nearly ¾ of those for mercury; more accurately half the square root of 2, that is, 0.707.

All the critical points for materials of different densities will be found to be on the same horizontal line, which represents a depth of about one-third of the total. Hence for this imaginary case of circular cross-sections, the critical point is always reached when the level has been lowered to about one-third of the total, no matter what the density is.

Suppose the original height of the liquid was only half as great, that is 5 cm. The hydrostatic pressures at proportionate depths will be only half as great, and the cross-sections one-quarter; hence the critical current, which from that formula is proportional to the square root of their product, will be only about one-third as great; more accurately, the square root of one-eighth, this is, 0.37. The critical point is therefore reached with relatively very much less current in shallow channels than in deep ones; or in other words by doubling the depth of the channel the limiting current will be much more than doubled, nearly trebled.

Fig. 4 and the deductions above made from it, apply rigidly only to the case to which that formula refers, namely to circular cross-sections of the contracted part. The analysis was made on this imaginary basis because a circular section is the only one

for which a formula existed, and therefore the only one for which the quantitative laws of the phenomenon could be accurately calculated and analyzed. The corresponding formula for the more common rectangular channels would, even if it existed, be likely to be much more complex and therefore less adaptable for studying the general laws.

In the absence of the mathematically correct formula for rectangular cross-sections, the following approximate deductions may be made for such cases from the one above for circles.

There are three important differences between circular and rectangular sections. It is probably safe to say that the pressure at the center of a rectangle is always less than at the center of a circle, for the same current and area, because the mean distances between the current elements is least in the circle; or in other words, for rectangular sections it takes a greater current to overbalance the hydrostatic pressure; hence for about the same depth of liquid a rectangular channel will stand a greater current before rupturing, than a circular one of equal area.

The second difference is that the areas of the cross-sections diminish in proportion to the height instead of the square of the height, as when circular. Hence lowering the level a given distance will not increase the current density so rapidly in rectangles as in circles in which the section shrinks both in width and height. Therefore the critical current will not be reached as abruptly, hence for relatively strong currents the column will not be so sensitive to rupture due to mechanical disturbances or to a slight increase of current.

The third difference is that for the same cross-section the channel may be made high and narrow thereby increasing the hydrostatic pressure for the same area of section.

However complex the general law may be for a rectangle, it is certain that when the section is a square or nearly so, no great error would be committed by assuming that the pressure at the center would be very nearly the same as that at the center of a circle of equal area, and whatever the error is, it is on the safe side; hence approximate results sufficiently accurate for practical purposes may be obtained from the Northrup formula when the section is approximately a square. And as the

important feature in the quantitative study of this phenomenon is that part of the current curve just at and above the critical point, let us assume such proportions of a rectangular channel that the contracted section will be approximately a square when the current is just at the critical point. It is of absolutely no importance in practice what the exact shape of the current curve is below this point, that is, after the rupturing contraction has started, and it is of very little interest what its shape is long before this point is reached. Hence it will suffice for all practical purposes to deduce this curve only for the immediate

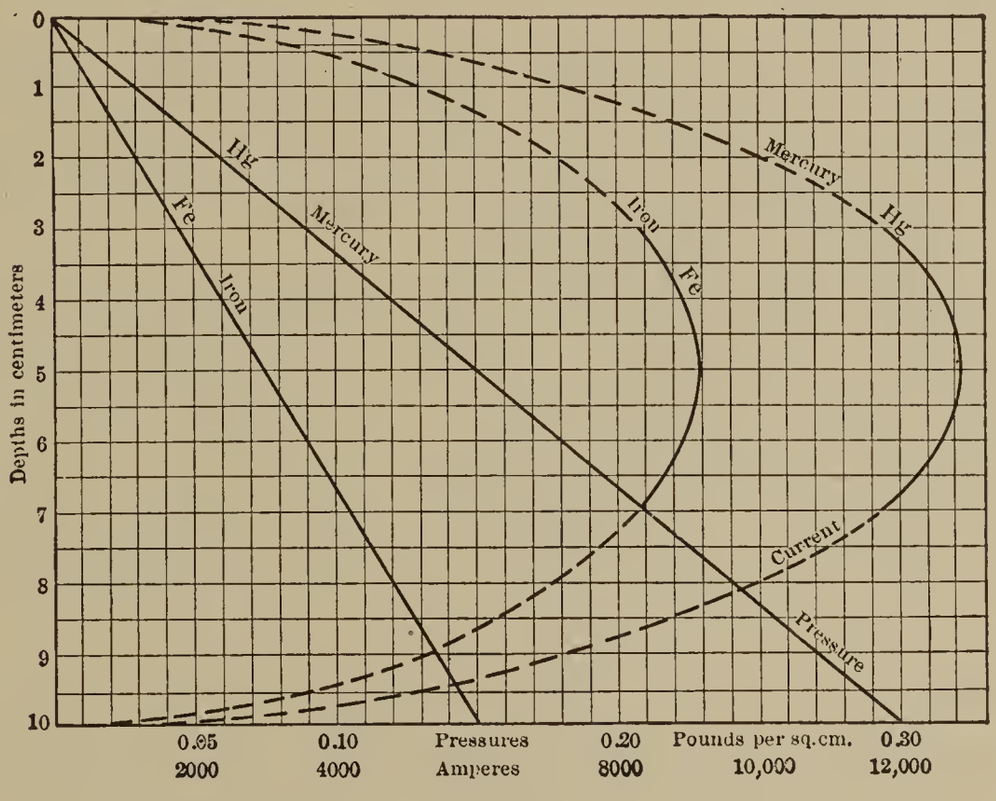


FIG. 5.

vicinity of the critical point, and this can be done with no great error by means of the Northrup formula.

Some trial calculations show that when the width of the conducting column is made half of its original height, then the critical current will flow when the cross-section has been contracted by the "pinch" effect to just one-half, and the cross-section is then a square. Hence when the cross-section of the original conductor is a rectangle whose height is twice its width, the following useful deductions may be made.

The curves in Fig. 5 give the actual figures for a rectangular channel 10 cm. deep and 5 cm. wide, when the conductor is mer-

cury. The scales and co-ordinates are the same as in Fig. 4. The straight line *Hg* gives the hydrostatic pressures at the various depths. The current curve *Hg* is shown dotted where its shape is not known, and in full where it can be calculated with close approximation by the Northrup formula.

It will be seen that the critical point is reached when the contraction has lowered the level to 5 cm., just half the original depth. The maximum current then is 12,900 amperes. Moreover the contraction increases very rapidly just prior to this current, hence it would begin to be unsafe long before this level has been reached.

If the Northrup formula can be assumed to apply in practice with sufficient accuracy to any shape of rectangular cross-section, that is, to deep and narrow or to wide and shallow channels, it can be shown that in any of them the critical contraction is at one-half of the original height.

The effect which the density of the conductor exerts is shown by the pair of lines marked *Fe,* which are for molten iron, the density of which, 6.88, happens to be just about half that of mercury. The hydrostatic pressures will therefore be one-half as great, but as the electromagnetic pressures vary as the squares of the currents, the currents for the iron will not be half as great but half the square root of 2, times as great, that is, .707 times or nearly three-quarters. Hence small differences in density will make still smaller differences in the current. If G and g are the densities of two different materials, C and c the respective currents, then the general formula for correcting for density is:

$$\frac{c}{C} = \sqrt{\frac{g}{G}}$$

If the section is made twice as high and wide, the critical current for mercury will be 36,500 amperes. Or if half as high and wide, 4,560 amperes. This shows that the critical current increases much more rapidly than in proportion to the height; for double the height it is nearly three times as great (or more accurately, the square root of 8, which is 2.83, because the section is four times as great and the hydrostatic pressure twice as great, the current being proportional to the square root of their

product). In other words, this means that small furnaces are far more sensitive to rupture by the "pinch" effect than large ones, and that considerable safety is gained by increasing the depth. If H and h are two different heights of the original columns, and C and c the respective critical currents, the general law is:

$$\frac{c}{C} = \sqrt{\frac{h^3}{H^3}}$$

It will be found that for the same materials the current density at the critical points and in the contracted sections, are different for different sizes of cross section. For mercury they are 730. amperes per sq. cm. for the smallest of the above sections, 2½ x 5 cm.; 516. for the medium, 5 x 10; and 365. for the largest, 10 x 20. Hence the critical pinch does not occur at any definite current density as had been supposed. These figures show that the current density may be made considerably greater in small furnaces than in large ones, without danger. They are seen to be inversely proportional to the square root of the heights. If CD and cd are the critical (that is, the maximum possible) current densities in two different channels (the original height in all these cases being double the width) and H and h are the respective original heights, the general law is:

$$\frac{cd}{CD} = \sqrt{\frac{H}{h}}$$

It was shown above that the critical current and therefore the current density, varies with the square root of the density G, and it has just now been shown that this current density varies inversely with the square root of the original height H for rectangular sections in which the height is double the width. Hence

$$CD = K\sqrt{\frac{G}{H}}$$

in which K is a constant which is equal to the current density for the case in which G and H are equal to unity. This constant is readily calculated as above described, and is found to be 442, which is a purely mathematical constant and involves no empirical factor. This formula applies to the current density in the con-

tracted portion just at the point C, Fig. 5, where unstable equilibrium begins. In practice it is more convenient to have the formula apply to the cross-section before contraction, and as this is just double the other, the constant becomes 221. Hence

$$CD = 221. \sqrt{\frac{G}{H}}$$

in which the current density CD is in amperes per square centimeter in the original cross-section, and the height H (the original one) is in centimeters. Or

$$CD = 895. \sqrt{\frac{G}{H}}$$

in amperes per square inch and in inches.

This very simple formula therefore enables one to calculate the critical current density directly from the density of the material and the original depth of the liquid conductor. The only approximate factor which it involves, is the one due to the assumption that the "pinch" pressure at the center of a square is the same as that at the center of a circle of equal area, and it is believed that the error is quite small; it is on the safe side. It should be remembered that this formula is based on a rectangular cross-section whose height is double its width, but for other proportions not departing too greatly from these, it probably will be correct within all practical requirements, as it is not necessary to know this critical value very exactly, because the rupture of the circuit may have such serious consequences that it is wise to keep as far away from this danger point as possible.

When the width is exactly half the height, this formula may be further simplified, because then the original area of cross-section is equal to $\frac{1}{2}H^2$. Making this substitution the formula for centimeters becomes

$$C = 111. \sqrt{GH^3}$$

and that for inches becomes

$$C = 449. \sqrt{GH^3}$$

thus giving the critical current instead of the current density.

It should be remembered that the above analysis of this phenomenon is based on the static state shown in Fig. 3, which is the only one which lends itself to a quantitative mathematical investi-

gation. In a furnace the pressure in the core of the contracted part must not only balance the hydrostatic pressure, but must be sufficiently greater to force the liquid away as fast as it flows back from above; it must overcome frictional resistance of a liquid in a liquid, and at a velocity which for deep contractions and very mobile liquids may be quite high. Hence for this reason the actual critical current would be somewhat higher than that given by the formula, that is, the danger with a given current would in practice be less. On the other hand the viscosity of the fluid will diminish this difference again and make the conditions approach more nearly to the static; with very viscous or half frozen liquids it is possible that even less current will produce the rupture than under the static conditions; hence it is advisable in high current density furnaces, not to use the full current until the mass is quite fluid, that is, not to try to start a fusion too quickly.

To give some general idea of the order of magnitude of these critical currents, the following values have been deduced from these formulas for molten iron whose density is taken as 6.88.

For a small trough 2 inches deep and 1 inch wide the critical current would be about 3300. amperes. For 4 x 2, about 9400. amperes. For 6 x 3, about 17,000 amperes. About 75 per cent. of these values would probably be a safe working limit if the channel is quite uniform, if the surface of the molten liquid is reasonably free from floating, heavy, non-conducing materials and if the liquid is not too viscous.

Summary: The chief features of this phenomenon are:

The pinching action is purely electromagnetic, and applies equally well to direct as to alternating currents. It tends to force the fluid out of both the ends of the conductor chiefly at its central axis and parallel to the direction of the current.

The contracting force is a function of the current, and of the size and shape of the cross-section, and may be determined from these. It is independent of the voltage, resistance, watts, heat, temperature, length of channel, etc., except in so far as changes in these may affect the other quantities. The opposing force in a horizontal column is a function of the density of the liquid and of the depth of the axis of the contracted column. The actual

contraction which results also involves the viscosity, fluid friction, smoothness of the channel, weight of floating masses, etc.

In a given channel, every current will contract the column to two different levels; the upper one is stable, the lower unstable. When the unstable one is reached complete rupture necessarily follows. If the lower or unstable level is produced mechanically by outside forces, rupture also follows electromagnetically. For increasing currents the level falls very slowly, when they are small, then more rapidly, and when near the unstable level the contraction becomes very rapid for the same increments of current. At a certain critical current depending on the quantities stated above, rupture immediately takes place.

For circular sections the accurate quantitative relations are known (Northrup's formula). For rectangular sections whose heights are about twice the widths, the critical current can be pre-determined with close approximation by the method described in this paper. For departures from these proportions of the section, the same formula is believed to be sufficiently approximate to serve as general guide.

The rupturing phenomenon takes place only at relatively high current densities, hence need not be feared in ordinary low current density furnaces, except when local contractions can occur from other causes, in which case rupture is liable at that point. When rupture does occur the result is likely to be a frozen charge on a broken core, probably necessitating a dismantling of the furnace, unless the rupture will heal at once by opening the circuit for a moment and following it by a reduced current.

The critical current fixes a very positive limit which the current and therefore the temperature cannot exceed in such furnaces. It is greater the deeper the channel, the greater the density, the less the viscosity, the smoother and more regular the channel is, and the more free the surface of liquid is from heavy floating masses. The effect, if any, which the width of the channel has on the critical current density, is not yet known. For the same change in level (like that due to a floating mass) the danger is far greater in small or shallow than in large and deep channels.

Philadelphia, March, 1909.

APPENDIX.

Experimental Results. Since this paper was written, the writer has made some measurements of the rupturing currents in a series of small tanks, in order to determine the quantitative relations which exist in actual cases in which there is an almost violent agitation accompanying the phenomenon. These might be called the dynamic conditions or conditions of motion, to distinguish them from the static conditions or conditions of rest, discussed in the paper, and which are the only ones for which the mathematical relations were known. Under the dynamic conditions, which represent those in actual practice, the force must be great enough not only to balance the hydrostatic pressure, but enough greater to move or squirt the liquid away from the contracted part faster than it can flow back from above. The questions of interest in practice therefore are: How much greater will the critical current be than that under the static condition assumed in the paper; and whether the relations between the quantities are changed.

The tests had to be made on a rather small scale, hence such factors as the surface tension (which is quite high for mercury), the friction on the walls, the errors due to the meniscus, the raising of the higher level by the metal displaced at the contracted part, etc., all became relatively much greater than they would be under the more usual conditions met with in furnaces. Moreover, the heating at such high current densities is so great that the readings had to be made very rapidly, therefore not allowing time for accurate adjustments.

Hence the numerical results are only approximate, but they are thought to be sufficiently accurate to serve as a useful guide until the tests can be repeated and extended by someone having the facilities for doing so under conditions approaching more nearly those of actual furnaces. Great accuracy in determining this danger point is, however, not necessary, as the consequences of a rupture may be so serious that one should keep as far below this critical current as practicable.

Four small tanks, *A, B C* and *D,* were constructed about as shown in the small diagram, *T,* on the adjoining curve sheet,

Fig. 6. Each tank was made of two lantern slide cover glasses about 3 inches by 4 inches separated by a V-shaped piece of glass and two strips of brass projecting at the bottom, which dipped into mercury cups to lead the current into and out of the mercury which was filled into the space between the glasses to various heights. The "pinch" was thus made to take place

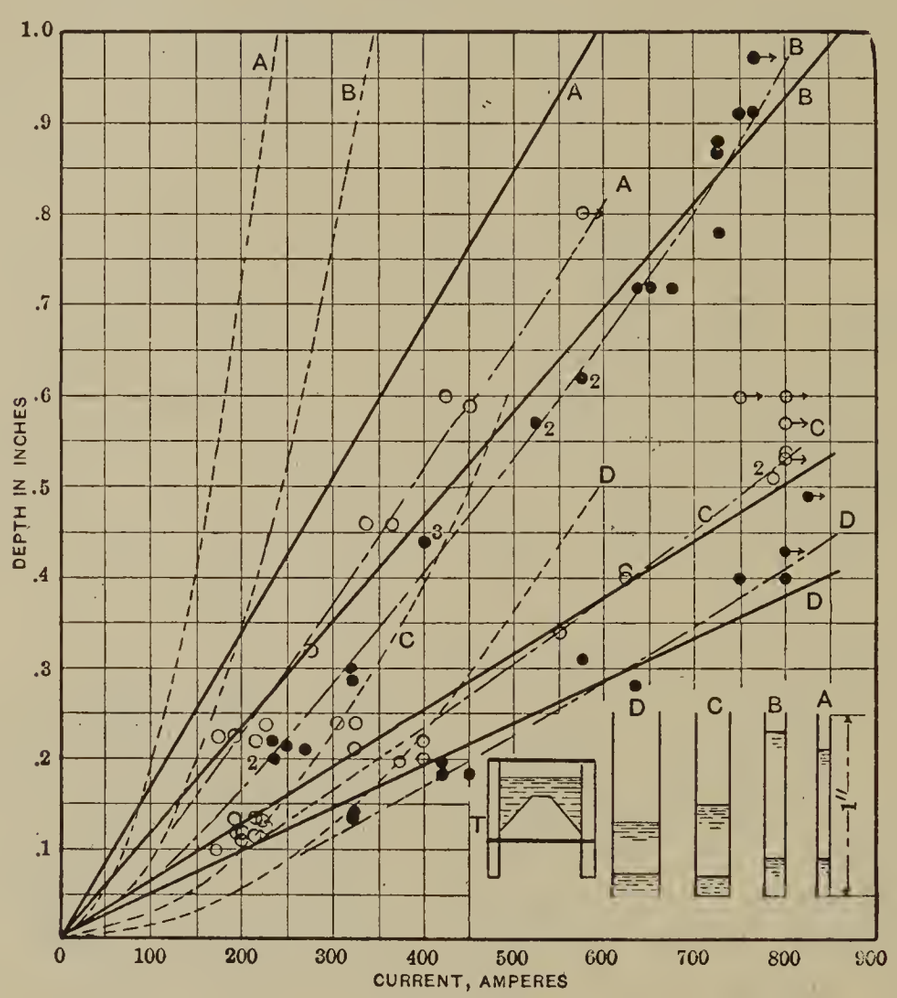


Fig. 6.

at the shallow part in the middle where the original depth of mercury could be read off on a scale pasted on the outside. Each test consisted in finding the current which would cause rupture at each of various depths. The mercury heated so rapidly that the current could be left on for only a few seconds, and the tanks had to be cooled off after each test.

The inside widths of the tanks, *A, B, C* and *D,* were roughly 1-16, 1-8, 3-16 and 1-4 inch respectively; accurately 0.071, 0.105, 0.193 and 0.254 inch. They are shown in section to scale and nearly three-quarter size, in the lower right hand corner on which are also indicated the ranges of levels of the liquid within

which the tests were made, therefore showing the proportions of the heights and widths. Tank *A* broke with the heat, but the others were run to as great a depth as could be ruptured with the source of current used, namely, about 800 amperes. The tests were made in the well equipped laboratory of the Leeds & Northrup Co., the facilities of which were very kindly extended to the writer for this purpose.

The results of the best of about 100 tests are given on the accompanying curve sheet, in which the vertical distances are the original depths (before the current is passed) in fractions of an inch, and the horizontal ones are the rupturing currents in amperes. Those for the tanks *A* and *C* are shown by small circles near the dash-dotted lines *A* and *C* respectively, while those for the tanks *B* and *D* are dots near the dash-dotted lines *B* and *D*, these lines having been drawn through what appeared to be the mean or most probable values.

To obtain the correct mathematical equations of these curves, especially a general equation for them all, would be a tedious task, and the results are not sufficiently accurate to make it worth while to do this. It is, however, possible to make some interesting and instructive deductions of a general and approximate character, including a very simple general formula which is probably sufficiently accurate for most purposes over the more usual ranges, and will serve as a useful guide to furnace designers until more accurate tests can be made.

The arrows pointing to the right mean that the current was not great enough to cause rupture, hence the true value is farther to the right. Numerals 2 and 3 mean that two and three tests respectively gave the same result. The rise of the higher level, due to metal displaced at the point of rupture, could not be measured, as the surface was highly agitated; in some places it rose high above the normal level, as though it were squirted up from below with considerable force. It took an appreciable time for the break to be completed, because the liquid had to acquire a considerable velocity and its inertia therefore had to be overcome. As the current could be kept flowing for only a few seconds on account of the heating, it is quite possible that the observed currents are a little higher than they would be in an actual furnace, in which the velocity of the liquid may be

acquired more gradually and in which the tanks are relatively much longer and therefore will have the upper level of the liquid less affected by the displaced liquid.

Taking all these factors into consideration, the current readings were probably too high, especially for the narrower tanks.

The dash-dotted curves are drawn through what were considered the fair mean values. The dotted curves are those obtained from the formula for the current density given in the paper and based on the static conditions, and on the assumption that the original depth is twice the width. In the present dotted curves this formula is extended to apply to all proportions of height to width; this may not be quite correct, hence one should not lay too much weight on these dotted curves beyond their proper range.

It will be seen that these two sets of curves depart rather rapidly from each other as the currents or heights become greater. Hence the formula given in the paper is quite safe for the higher values, and, in fact, more than safe, as the critical currents for the greater depths may be assumed to be considerably greater without great danger.

This is readily explained by the fact that the deeper the channel the greater must be the velocity of the metal which is squirted or squeezed out from the contracted part, and this velocity does not enter into the formula given in the paper for the static conditions. Moreover, the surface tension also becomes relatively much greater for greater depths, especially in such narrow channels, and as this and the friction on the walls are both less in larger and wider channels, the values for the critical currents in actual furnaces will probably lie somewhere between these two curves.

All four of the dash-dotted curves, moreover, approach much more nearly to straight lines than do the dotted curves, which are parabolas. Hence the relations between the quantities in the formula given in the paper have also been changed, the current being more nearly proportional to the height than to the square root of the height. Increasing the depth, therefore, has a greater effect on increasing the critical current than under the static conditions.

These approximate straight line relations, and the fact that the

critical currents appear to be roughly proportional to the widths, suggested to the writer that a single, very simple and general formula could be deduced from these tests, which would apply to all the tanks, and therefore would probably not be very incorrect for the ordinary cross-sections occurring in actual furnaces. As great accuracy in the predetermination of this danger point is not necessary, owing to the fact that it ought not to be approached too closely, it is believed that this approximate formula will serve a useful purpose until the complicated quantitative laws can be more accurately determined by experiment.

This general formula was found to be

$$CD = 2240 \sqrt{G}$$

in which CD is the current density in amperes per square inch, and G the specific gravity. Or

$$CD = 347 \sqrt{G}$$

in amperes per square centimeter.

This means that approximately there is a certain current density for every material at which rupture will occur. For iron this would be 5,880 amperes per square inch, or 910 per square centimeter. For deep and narrow or shallow and wide channels this no longer holds.

The values obtained from this formula are represented in the curve sheet by the straight heavy lines. It will be seen that except for very deep and narrow, or very shallow and wide channels, they agree approximately with the dash-dotted curves. The difference is greatest for the very narrow channel *A*, but in this the friction on the walls was undoubtedly abnormally great, and therefore the observed critical currents were greater than they would be in normal cases; hence the difference between the two curves is in the right and the safe direction. In general the values obtained from this approximate formula become too high as the channels become deeper, and too low (that is, on the safe side) as they become shallower.

It would follow from this formula that the width of the channel has approximately no effect on the critical current density, or, in other words, that the critical current increases in direct proportion to the width. It would also follow that for a given

area of cross-section the critical current would be the same whether the channel were made deep and narrow or wide and shallow. The curves show, however, that neither of these deductions are quite correct, especially for the extreme proportions.

As the maximum temperature is generally the important criterion in such high current density furnaces, it may be of interest to see how the conditions for maximum temperature and those for the greatest critical current compare with each other. Let it be assumed at first that the loss of heat through the walls and electrodes is independent of the proportions of the channel, and that the temperature is proportional to the watts per cubic inch in the resistor. Substitute for the watts the expressions for the resistance and the square of the current, the former in terms of the height, width, length and resistivity, and the latter in terms of the height, width and specific gravity, as obtained from the above formula for the maximum current density. It will then be found that the temperature is independent of all the variables, being proportional merely to the product of the resistivity and the specific gravity. Hence under these assumptions the temperature cannot be increased by any relative changes in the length, height or width of the channel.

But the critical current density does not follow the above equation exactly, as it is slightly greater for the smaller heights and less for the greater heights. Hence there seems to be a slight advantage in making the channel shallow and wide, when the maximum possible temperature is desired; in other words, there is no gain and even apparently a slight loss in making the channel deep, although at first thought one would suppose that the deeper the channel the less the liability to rupture, because the hydrostatic pressure is then greater.

The explanation of this apparent anomaly is that the maximum current seems to increase in proportion to the width, but not quite in proportion to the height; hence it is better to increase the width than the height. However, the differences seem to be small, and to determine the question definitely will require more accurate tests. The only definite conclusion which can be drawn at present appears to be that changes in the proportion of the height and width seem to have only a small influence on the maximum possible current density, and that therefore the

best possible shape of a rectangular cross-section probably depends on other considerations like the loss of heat, which is least when the cross-section is a square.

Another factor which may be even more important than the above is the one stated in the conclusion of the paper, namely, that the shallower the channel, the greater is the danger due to the contractions caused by obstructions or floating masses. The length of the channel also becomes an important factor if, with a relatively deep channel. it can be made so short that the material displaced by the pinching effect piles up very high on both sides so that the hydrostatic pressure is rapidly increased; the critical current densities ought then to be very much higher. Confining the material in a covered channel, or using an external magnetic field, ought also to enable higher current densities to be reached.

The tests also confirmed the theoretical deduction that there are two levels corresponding to each current, the higher one being stable and the lower one unstable. If for a relatively small and safe current the level was further depressed by inserting an insulating body, rupture immediately took place.

DISCUSSION.

DR. NORTHRUP: When Mr. Hering tested the critical current which would rupture, he found that, with the small mercury channels which he used, it took a somewhat larger current to produce rupture than is required by his mathematical formula. Well, it seems to me, after seeing his experiments, that the reason is clear for this. In dealing with small channels containing mercury, as in the experiment, the forces of surface tension are great and tend to maintain the surface of the mercury level. The current has not only to overcome gravity in depressing the level, but it has to overcome the pull of surface tension which tends to restore the level. I am, therefore, inclined to think that his formulæ, derived from theoretical considerations as applied to large furnaces, are to be relied upon even more than his measurements, which were made with small mercury channels only.

Mr. F. A. J. FitzGerald: The largest scale on which I have seen the "pinch" phenomenon working is in the induction furnace. The American Electric Furnace Co. had a small 60 kw. furnace at their plant in Canada, and we made an attempt to use it for melting aluminum. What practically brought the experiments to an end was simply this "pinch" phenomenon. We even ran the aluminum to a depth of six or seven inches in the furnace, the width of the vat being about ten inches, and on every occasion where we could get the temperature of the metal up just a little bit above the melting point, then the "pinch" phenomenon would occur and the circuit would break. It would just hold the metal molten and that was all. We have also with this furnace, by working with a very shallow bath of steel, been able to get the "pinch" phenomenon in that case. We tried the experiment on a larger furnace holding about 2,000 pounds of steel, but the amount of power at our disposal was not sufficient to produce it. If anybody wanted to make experiments on a large scale, as has been suggested, I imagine that the induction furnace would be a suitable apparatus with which to carry it out. I think it would be interesting to inquire of Mr. Hay, or to try to find out, if in the Röchling-Rodenhauser furnace, where they apparently use very high current densities in the induction channels, the "pinch" phenomenon ever occurs.

Mr. Hering: I have had it occur repeatedly in channels filled with molten iron to a depth of six inches. The column would snap off every time. I could hardly get the metal melted before it would snap off. Of course, the proper way to do is to heat it more slowly; I tried to heat it too fast. I did not know then what I know now about the cause of this contraction. I think Dr. Northrup is right in saying that surface tension plays a much more important part in the small channels that I used in these tests than it would in the larger channels in practice. If that is the case, the figure I gave in the appendix to my paper is too high. It is safer, therefore, to keep considerably below that figure, because in actual practice it may be somewhat lower. But any one who has encountered that phenomenon will keep away from it as far as possible; it is well not even to approach it too closely. Very accurate figures are, therefore, not necessary.

A paper presented at the Fifteenth General Meeting of the American Electrochemical Society, at Niagara Falls, Canada, May 6, 1909; President E. G. Acheson in the Chair.

FURNACE ELECTRODE LOSSES.

By C. A. Hansen.

Most electric furnaces are fitted with carbon or graphite electrodes of one shape or another, and a large proportion of these electrodes are water cooled at the cable contacts, since otherwise it is usually difficult to maintain good electrical junctions. Since one end of the electrode is hot and the other end is cold, there is a flow or loss of heat into the cooling water, which must be supplied electrically. In addition we have also a C_2R loss in the electrode itself. It is to these losses I wish to refer in this paper. So far as I know, there is at present nothing in the literature from which one can get any idea as to their magnitude.

According to FitzGerald (Electrochemical Industry, V, 451) the heat conductivities of carbon and graphite are as 1 to 18. According to other published data (Lincoln) the ratio of resistances is about 3.8 to 1. It is therefore reasonable to assume that the losses in two similar furnaces, fitted with carbon and graphite electrodes respectively, will differ from one another. If we assume equal differences in temperature to exist between the hot and cold ends of two electrodes, respectively of carbon and graphite, we should expect to find the graphite to be the more efficient when the difference between the C_2R losses exceeds the differences between the heat conductivity losses.

I shall detail a few experiments in which I consider that carbon and graphite electrodes were used under comparable conditions.

Run No. 1.

In June, 1907, in the course of some resistance furnace experiments on the manufacture of titanium carbide, a furnace was constructed similar to that shown in Fig. 1. This furnace was about 6 feet x 3 feet x 3 feet inside dimensions, and was fitted with 8″ x 8″ graphite terminals built up of 40″ x 4″ x 4″ Acheson mater-

ial (detailed in Fig. 2, A.) A characteristic log of this furnace follows:

RUN NO. 1—TITANIUM CARBIDE FURNACE.
June, 1907.

Time	Volts	Amperes	Kw.	Kw. Hours	Electrode Loss		Remarks
					Kw.	% Load	
9.30	44	. . . .	5	. . .	. . . .	. . . .	Start.
10.15	44	. . . .	6	. . .	. . . .	. . . .	
11.15	44.4	. . .	7	. . .	. . . .	. . . .	
12.15	45.5	. . . .	20	. . .	. . . .	. . . .	Increased voltage to start.
12.35	90	. . . .	45	. . .	. . . .	. . . .	
12.45	65	550	45	. . .	. . . .	. . . .	
.55	55	1200	75	. . .	. . . .	. . . .	
1.05	42	1350	60	. . .	1.57	2.6	
1.15	36.5	1400	57.5	. . .	2.51	4 4	
1.25	43	2130	92.5	. . .	5.03	5.45	
1.35	44	2960	122	. . .	6.91	5.67	
1.45	40.7	3500	160	. . .	11.6	7.2	
1.55	40	4300	188	. . .	12.25	6.5	
2.05	39	5000	270	. . .	15.0	5.6	
2.15	38	5750	245	. . .	21.03	8.3	
2.25	37.5	6200	260	. . .	24.5	9.4	
2.35	34.8	6900	280	. . .	27.9	10.0	
2.50	33 4	7500	287.5	350	31.4	10.9	
2.55	33	7650	295	. . .	33.0	11.2	
3.05	30.5	8500	300	400	. . . .	. . . .	
3.25	26	9600	300	. . .	. . . .	. . . .	
3.35	25	9500	285	. . .	45.3	15.9	
3.45	24	9850	275	730	47.2	17.2	
4.00	23	9950	270	. . .	50.3	18.6	
4.10	23	10000	275	900	55.0	20.0	
4.15	. . .	. . . .	. . .	. . .	. . . .	. . . .	Shut down.
4.17	. . .	. . . .	. . .	. . .	45.5	. . . .	
4.18	. . .	. . . .	. . .	. . .	40.8	. . . .	
4.22	. . .	. . . .	. . .	. . .	31.4	. . .	
4.30	. . .	. . . .	. . .	. . .	25.1	. . . .	
4.40	. . .	. . . .	. . .	. . .	22.0	. . . .	

RUN NO. 2.

In January, 1909, a similar furnace, 28″ by 30″ by 5′, was built for some special graphite experiments. The electrode details were exactly the same as in the first case here recorded, with the exception that, in place of graphite, carbon electrodes were substituted. These 8″ x 8″ carbon terminals were built up of four 4″ x 4″ carbons each (National Carbon Co. material). After giving the electrodes three or four regular runs, to season them, a water record was taken, with the following results:

Run No. 2—Graphite Furnace.

January, 1909.

Time	Volts	Current Amp.	Kw.	Kw. Hours	Kw. Loss Electrodes	
9.00	45	. . . .	. . . .	. . . .	. . . . .	Start.
9.45	43	3500	150	. . . .	. . . . .	
10.10	41	5000	205	. . . .	. . . . .	
10.35	43	6000	258	. . . .	. . . . .	
11.10	40	8000	320	. . . .	. . . . .	
11.25	38	8400	320	. . . .	20.3	
11.32	36	9200	330	. . . .	22.2	
11.40	35	9600	336	. . . .	23.1	
11.47	34	9600	326	900	24.3	
11.50	. . . .	. . . .	. . . .	. . . .	. . . . .	Shut off.
11.52	. . . .	. . . .	. . . .	. . . .	14.7	
11.55	. . . .	. . . .	. . . .	. . . .	12.8	
12.00	. . . .	. . . .	. . . .	. . . .	10.8	

The temperatures near the electrodes within the furnace were determined by a method to be described later, and in both cases were found to be in excess of 3,000°. In other respects the electrodes were subject to the same conditions, viz., the same current, the same relative dimensions, approximately the same heat capacity in each furnace and approximately the same power curves. The maximum electrode losses were only 24.3 kw. with carbon electrodes as against 55 kw. with graphite electrodes. The electrodes were comfortably cool to the touch where they protruded from the water jackets. There was no local heating in any case, so it is safe to assume that contacts between water jacket and electrode do not explain the difference. Furthermore, the results have been repeatedly checked in similar charted runs on these same furnaces.

Run No. 3.

I shall detail one more run before attempting to analyze the data given. Continuing the titanium carbide work, the furnace was enlarged so that at present it has the dimensions given in Fig. 1. It will be noted that the end walls, through which the graphite electrodes project, have been increased in thickness from 9″ to 13″. A slight difference has also been made in the shape of the carborundum packing, which separates the electrodes from the wall.

See detail Fig. 2B. The object of increasing the carborundum packing was merely to add to the end wall protection, while the wall thickness was increased merely to give it greater stability,

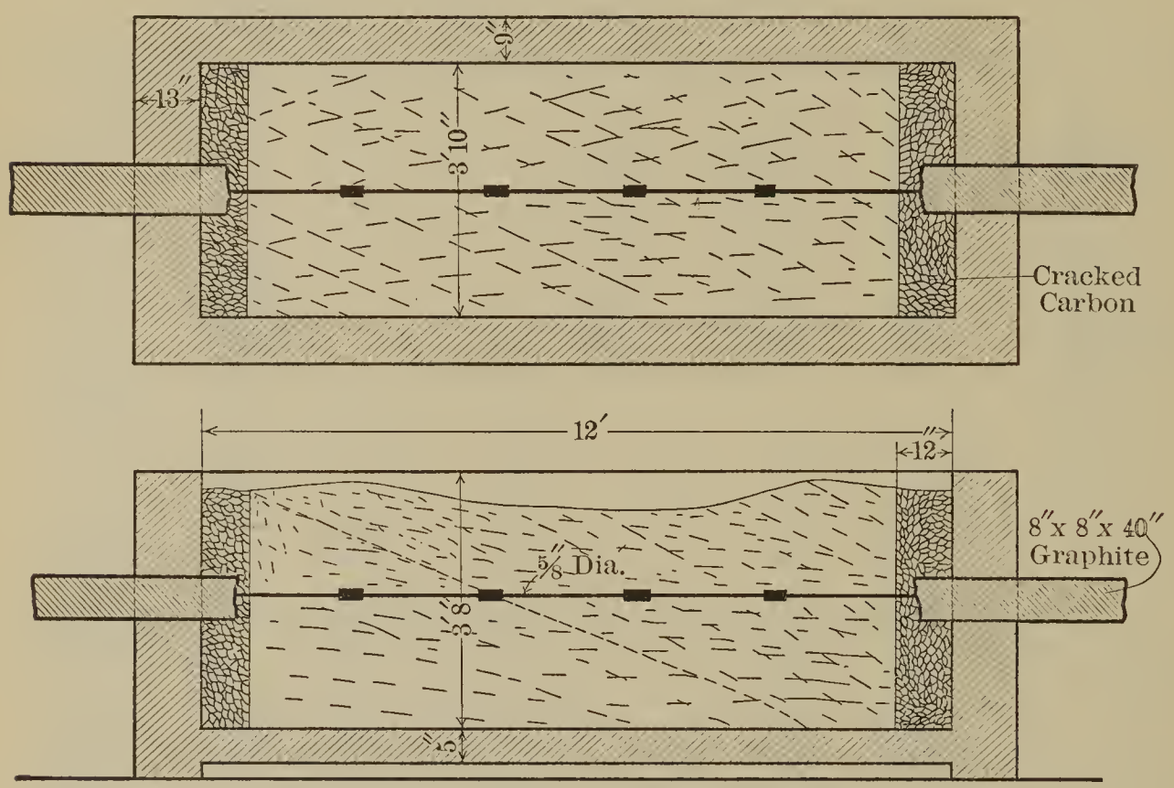


FIG. 1.

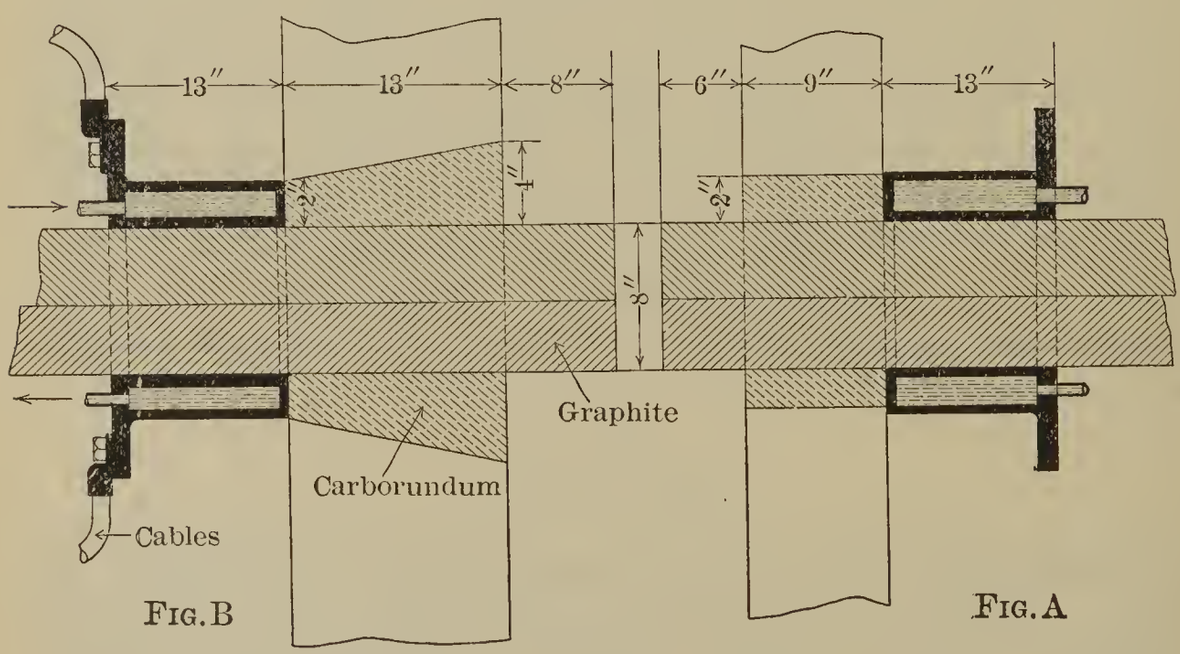


FIG. 2.

since it was intended to be permanent. In the characteristic log of the new furnace, which is here given, I have taken the electrodes separately to show how they check one another. The elec-

trodes are, of course, as nearly alike as one would ordinarily get them in practice.

RUN NO. 3—TITANIUM CARBIDE FURNACE.
October, 1908.

Time	Current	Volts	Kw.	Kw. Hours	Loss in Electrodes				Remarks
					Kw. No. 1	Kw. No. 2	Kw. Sum.	% Load	
8.00	. . . .	90	. . .	. . .	. . .	. . .	.	. . .	Start.
9.00	2800	. . .	225	27	2.2	2.0	4.2	1.9	Changed to 45 V. 9.20.
9.30	6250	40.5	250	178	3.5	4.9	8.4	3.4	
10.00	8880	39.0	330	323	8.1	10.3	18.4	5.6	
10.30	9700	36 5	350	520	12.0	15.0	27.0	7.7	
11.05	12000	35.5	380	700	15.3	17.7	33.0	8.7	
11.45	13800	33.0	420	940	21.3	19.7	41.0	9.8	
12.20	14000	34.0	450	1250	23.5	24.3	47.8	10.6	
1.00	14000	34.0	425	1505	25.4	26.0	51.4	12.1	
1.30	14500	32.0	415	1920	27.6	28.1	55.7	13.4	
2.30	14500	32.0	420	2128	26.6	23.3	49.9	11.9	
3.00	14500	32.5	430	2370	29.1	27.9	57.0	13.2	
3.30	14500	31.7	410	2600	27.9	26.9	54.8	13.4	
4.00	14500	31.3	400	2780	29.1	27.0	56.1	14.0	
4.35	14500	33.0	445	3034	28.9	26.5	55.4	. . .	Shut off.
4.40	. . . .		. . .	. . .	21.3	19 4	40.7	. . .	
4.55	. . . .	. . .	. . .	. . .	19.1	16 6	35.7	. . .	
5.00	. . . .	. . .	. .	. . .	17.8	16.6	34.4	. . .	
5.18	. . . .	. . .	. . .	. . .	15.0	12.4	27.4	. . .	

The striking result in the last run is the fact that, although we have increased the effective resistance length of electrode, and have increased the current density so that the C_2R losses should be more than doubled, the total electrode loss has not been increased over that of the first run. Assuredly then, we have increased efficiency by increasing the length of the electrode imbedded in the wall.

It was thought that we might be able to separate the electrode losses into resistance and heat conduction components by simultaneous equations, using the results obtained in the graphite electrode runs. Heat conduction would be inversely proportional, roughly, to the length of the conductor, in this case from some point on the electrode within the furnace to some point within the water-cooled terminal, *provided the same temperature gradient held for both electrodes in question.*

Let us take the two graphite electrode runs. Very different current densities prevailed in the electrodes of the two furnaces,

when the temperatures at the electrode tips were actually comparable, *i. e.*, toward the end of the runs, and the temperature gradients could not be considered comparable. The simultaneous equation procedure was, therefore, abandoned without trial. The attempt was, however, made to separate the losses roughly by applying such measureable constants as could be obtained.

The average resistance of the 4″ x 4″ x 40″ Acheson graphite used in this work, was 0.000684 ohms per inch cube, and at 1,500°, the average temperature of the electrode, this resistance falls to

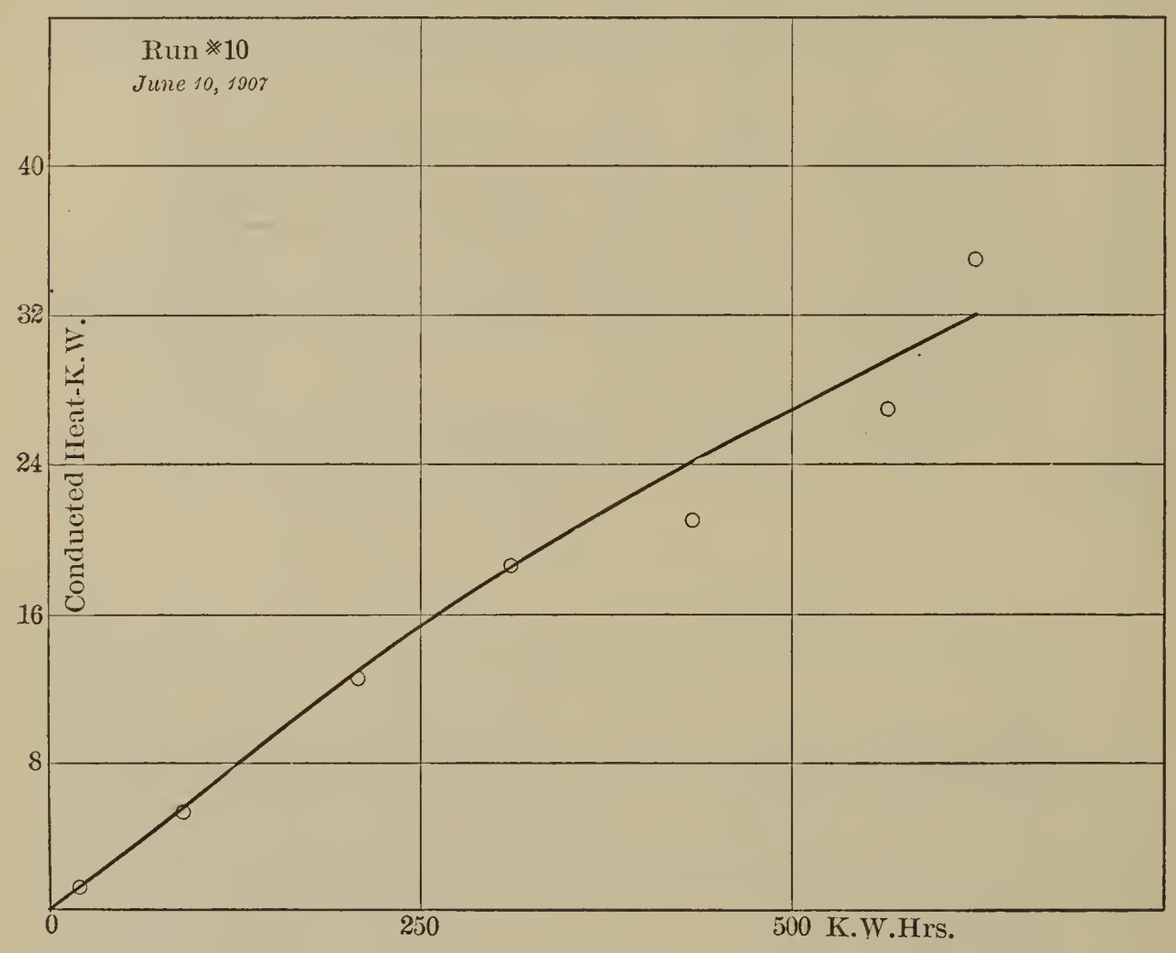


FIG. 3.

about 60 per cent. of that value. The effective resistance of each electrode in furnace No. 1 was taken as 16″ (one-third the length of the water-cooling jacket, plus the wall thickness, plus one-half the distance the electrode projected into the furnace). The reasons for not taking the entire electrode length are, of course, obvious, but the fractions used are purely arbitrary. At any rate, using the 16″ length and the 60 per cent. cold resistance, we get a total electrode resistance for No. 1 furnace of 0.0002 ohms, cor-

responding to a C_2R loss of 20 kw. at 10,000 amperes. With this value given, the maximum loss in run No. 1 was separated into 20 kw. C_2R loss and 35 kw. conducted heat, and working back, *i. e.*, calculating C_2R and substracting from the total loss found, I obtained data for plotting conducted heat against useful kw.-hour input. The kw.-hour input should, in a way, be proportional to the temperature within the furnace and, in a way, the conducted heat should be proportional to this temperature. The curve, Fig. 3 in which these results were plotted, is interesting, in so far as its shape corresponds with what we expected to find. Let us apply the same reasoning to the electrode losses in furnace No. 3.

Effective length No. 1 electrode = 16 inches; resistance 0.000100 ohm.

Effective length No. 3 electrode = 22 inches; resistance 0.000137 ohm.

C_2R loss for No. 1 per electrode at 10,000 amps. = 10.0 kw.
C_2R " " No. 3 " " " " amps. = 13.7 kw.
C_2R " " No. 3 " " " 15,000 amps. = 30.7 kw.

Assuming for the moment a heat conductance inversely proportional to length of conductor, we get

No. 1 conducted heat per electrode = 17.5 kw.
No. 3 " " " " = 12.75 kw.

The total loss for No. 3 electrode, at the end conditions of the furnace run, *should,* therefore, be 43.45 kw., as against 27.5 kw. for No. 1 electrode at the end conditions obtained in that run. The maximum losses (total, both electrodes) should have been 86.9 and 55 kw. respectively.

Now we found that the cooling water in No. 3 furnace did actually carry off less than corresponded to the C_2R loss alone, as we here calculated it—only 57 kw., actually measured as against 61.4 calculated as C_2R loss[1].

The inference is of course that the electrode is at least as hot as the furnace interior by reason of the C_2R heating and not alone blocking the flow of heat from the furnace outward it actually feeds heat in both directions the main portion naturally going to

[1] The 60 per cent. cold resistance figure used in these calculations comes near the inversion point in resistance—temperature co-efficient curve and is therefore lower than we should have used. In addition, we have neglected contact resistance between electrode and terminal block. Correcting for these errors, we would obtain a calculated result that agrees even less well with observed values.

the cooling water jacket. If we examine the run sheets previously detailed, we note that the electrode loss does not fall off markedly immediately after the current is shut off. The true conduction loss for an electrode not carrying current is, however, not measured by this value, because of the heat capacity of the electrode itself. It is useless to continue the analysis as regards carbon electrodes, since it is perfectly clear from the above where such an analysis will lead us when we assume a resistance for carbon 3.8 times that of the similar graphite electrode. I see no reasonable explanation for the results, at present.

It is but natural to infer that since the resistance loss in an electrode is proportional to the square of the current, and since also graphite has a lower resistance than carbon, that a current density would ultimately be reached at which the graphite electrode would be superior in efficiency to the carbon electrode of the same cross section. Here, however, in runs No. 1 and No. 2 we have reached current densities of 157 amperes per square inch which is not by any means a low current density in practice for graphite electrodes of this size. Still at this current density the carbon is certainly the more efficient electrode.

Since the furnaces in which these electrodes had been tested were not identical nor the charges identical, it was possible that I was wrong in making direct comparison. I therefore attempted, in a separate experiment, to make a test under conditions which would, without question give strictly comparable results. This run, as a matter of fact was made before run No. 2 (October, 1908), and the results of the run determined the choice of carbon electrodes for No. 2 furnace. I wanted however, first in this article to detail experiments carried out on a practical scale.

Run No. 4.

The furnace, 18″ x 18″ x 48″ inside measurements, was constructed of a single course of silica brick laid in fire clay and in the center of each of the four sides was fitted a 4″ x 4″ electrode (see Fig. 4). Each electrode was separated from the wall by a 1½″ layer of carborundum, put in with water glass. One of the end electrodes and one of the side electrodes were National Carbon Company stock, the other two electrodes, similarly placed, were Acheson Graphite Company stock. The water jackets were

identical, and in general the arrangement was such that a direct comparison could be made. The end electrodes were to carry current, and the side electrodes were intended merely to show comparative heat losses by conduction. The furnace was filled with cracked carbon, about 500 pounds of broken arc-lamp electrodes. This charge was chosen for its high resistance and for the reason that it does not decrease in resistance on heating to high temperature to anywhere near the extent that petroleum coke and its products do. Each of the water-cooled terminals was fitted with rub-

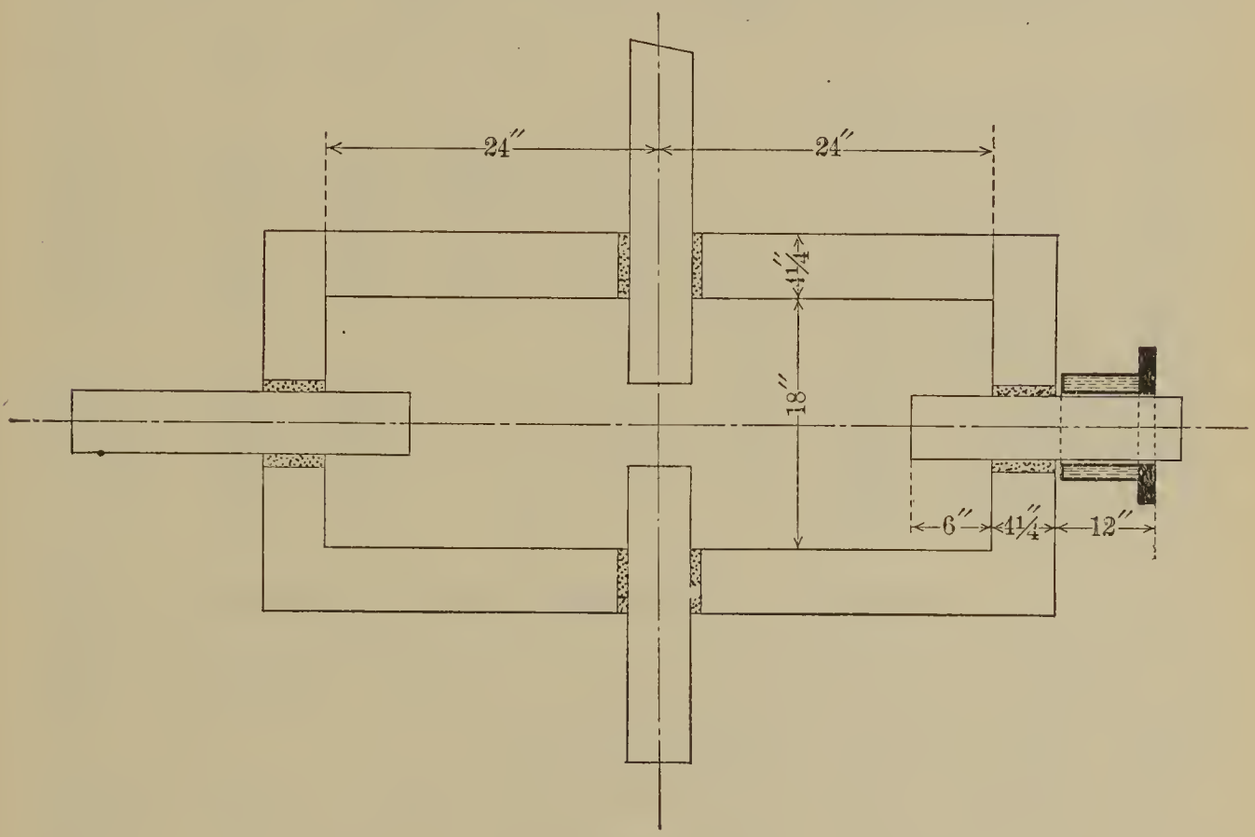


FIG. 4.

ber connections, and the tubes were brought out and fastened to a board in such a way that they would always be full of water. Thermometers were then merely let down into them. The rate of flow was determined by simply catching the overflow for a minute and weighing it.

The average flow and maximum temperature rise for the various electrodes are given below:

	Maximum temp. rise	Grams water per second
Carbon electrode (Carrying current)	19.2° C.	53.8
Carbon idler	7.7° C.	13.6
Graphite electrode (Carrying current)	19.7° C.	83.7
" idler	9.3° C.	96.4

The cold water temperature was 5.8° and varied only slightly during the run. The log of this experiment is also given in detail, and for the sake of making comparison easily between losses and the square of the current, a column headed $C_2 \times 10_{-6}$ is included.

RUN NO. 4—FOUR-ELECTRODE FURNACE.
October, 1908.

Time	Amps.	Volts	Kw.	Kw. Hours	$C_2 \times 10^{-6}$	Electrode Losses in Kilowatts			
						Carbon		Graphite	
						Elec.	Idler	Elec.	Idler
10.07	350	43.5	14	0	0.123	. . .	. . .	. . .	. . .
10.30	354	44.0	16	6	0.125	0.086	0.00	1.28	0.147
11.00	368	43.3	16	14	0.135	0·086	0.00	1.92	0.207
12.00	480	43.5	22	32	0.230	0.432	0.201	2.50	0.728
12.35	590	43.5	24	43	0.348	0.412	0.163	2.79	0.712
1.00	632	42.7	24	53	0.399	0.462	0.175	2.83	0.771
1.30	640	42.4	24.8	65	0.410	0.517	0.175	3.63	0.831
1.50	870	66	60	75	0.757	. . .	. . .	. . .	. . .
2.22	1060	67.5	68.6	100	1.124	1.015	0.215	3.77	0.750
2.37	1160	69	82.0	120	1.346	1.20	0.250	4.20	1.40
2.55	1400	69	92.6	150	1.960	1.43	0.283	4.60	2.56
3.20	2260	70	144.4	204	5.108	2.75	0.315	6.07	3.64
3.45	2520	69	168.0	262	6.350	4.37	0.445	6.98	3.58

The rise in temperature at the start was so small that undoubtedly large percentage errors were introduced. Towards the end, the quantities were all such that the percentage error was quite small. The loss data is plotted in Fig. 5.

Unfortunately, the run was interrupted before we had exceeded the current densities which had obtained in runs Nos. 1 and 2. The balance, at which both kinds of electrodes are equally serviceable, has therefore not yet been located experimentally. Analysis of the loss data indicates the existence of a balance at between 3,100 and 3,200 amperes for the No. 4 furnace,—a current density of 194 to 200 amperes per square inch.

The average ratio of losses for the 4″ x 4″ carbon and graphite electrodes at current ranging from 2,000 to 2,500 amperes, is 1 to 1.99. The average ratio of losses for the 8″ x 8″ carbon and graphite electrodes in runs 1 and 2, at the same current densities, is 1 to 2.03. It is therefore quite reasonable to assign the same current density of about 200 amperes as denoting the balance of efficiencies for the larger electrodes.

Temperature Estimations.

In making the run with the four-electrode furnace, I determined to see whether or not I could make use of some of the experience I had gained in previous research with carbons. For instance, I had obtained data covering pretty well the physical changes in some carbons with temperature, and it seemed at least

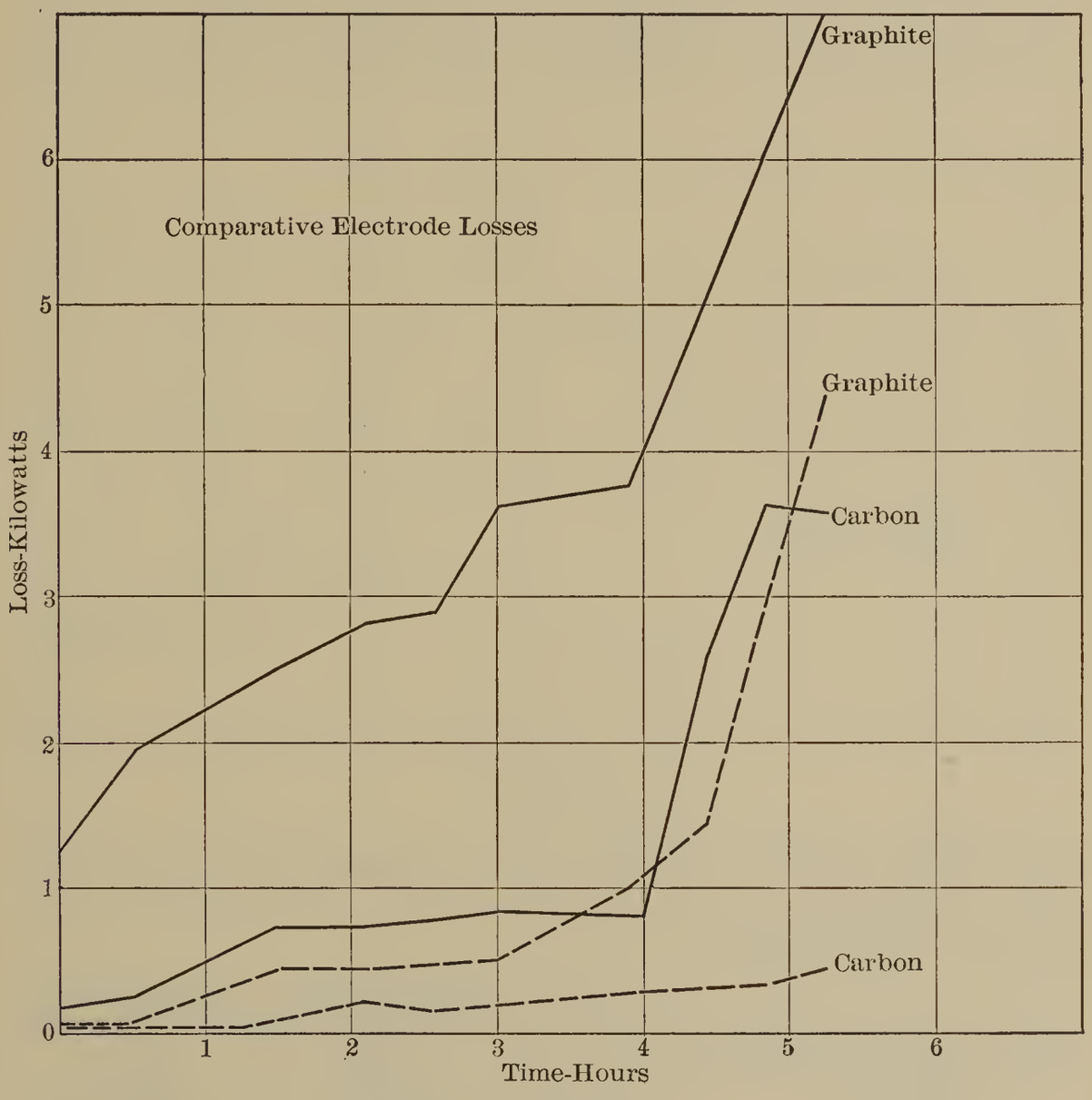


FIG. 5.

possible to work back and get at the maximum temperature which had obtained in various parts of the furnace.

Embedded in the charge I placed four small carbon motor brushes, which had previously been fired to 800° C. Two of them were placed flat against the tips of the idler electrodes, the other

two close to, but to one side of the current carrying electrodes. After the run these test brushes were removed and tested.

Three distinct temperature approximations could be made from each carbon; hardness by Shore sclerescope (See *Electrochem. and Met. Ind.*, VI, 422); electrical resistance by special apparatus designed for brush work; and absolute density, or "real density," as FitzGerald calls it, by weighing in benzol. Above 2,000°, the particular carbon used changes only slightly in absolute density and hardness, but the resistance is still practically a linear function of the temperature. The hardness and absolute densities, then,

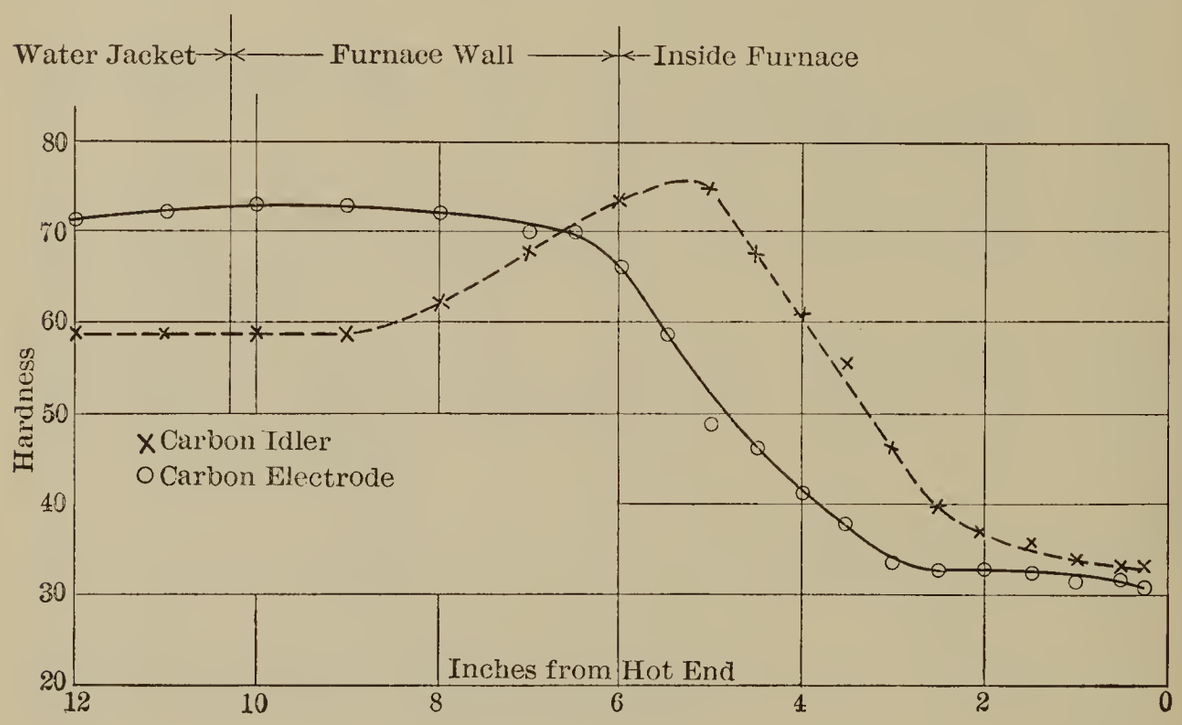


FIG. 6.

merely indicated temperatures in excess of 2,000° for each sample, while according to resistance determination, the following temperatures were obtained:

	Ohms per inch sample	Temperature defined by sample
At carbon electrode tip.....	0.000665	3230°C.
" graphite " "	0.000628	3300°C.
" carbon idler " "	0.000552	3500°C.[2]
" graphite " "	0.000835	2830°C.

[2] In giving 3500° for the temperature at the tip of the carbon idler, some explanation is necessary. The maximum temperature obtainable in this laboratory is derived from a graphite tube furnace in which a heater 12 inches long by 2½ inches outside and 1¾ inches inside diameter is surrounded by, but insulated from the carbon packing. After warming up for a considerable period at some 20 k.w., the power is increased to 50 k.w. for 20 or 30 minutes, then 75 k.w. until the tube fails—usually a matter of ten or fifteen minutes. There is every indication that failure is due to vaporization, and we have arbitrarily assigned 3500° as the temperature. The specific resistance of the particular test carbon so heated checks with the value given in the table.

The temperatures indicated by the samples at the electrode tips, as distinguished from the idlers, are somewhat lower than they should be, the samples being packed to one side to avoid vaporizing, due to local arcing, and so spoiling them for test purposes. The results obtained at the tips of the idlers are instructive, however,—we note that because of the excellent heat conductivity of the graphite idler the temperature at its tip is some 700° lower than at the tip of the carbon idler similarly placed.

Analysis of the carbon electrodes, after removal from the furnace, also leads to interesting conclusions. A slice ½″ thick and

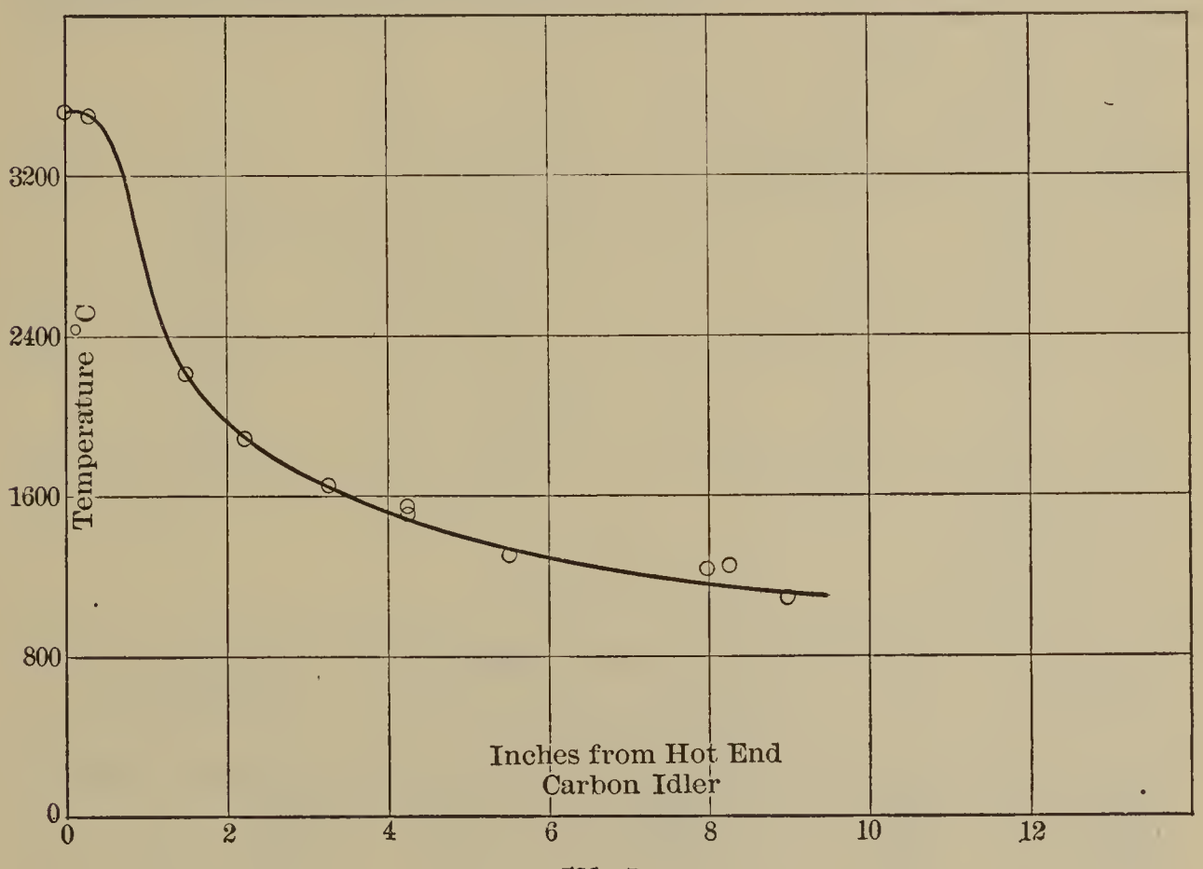


FIG. 7.

12″ long, was cut back along the side of each carbon. These slices were marked off into reference areas on the surface exposed by the cut, and these reference areas were tested on the sclerescope, with the results plotted in Fig. 6.

In addition, strips were cut out from a carbon idler at various distances from the hot end and perpendicular to its axis, for resistance and absolute density determinations. From these determinations I have tried to construct a hardness temperature diagram, by which I could interpret the curves shown in Fig. 6. The temperature estimates are all based on the assumption of a similar-

ity existing between the curves of hardness, resistance and absolute density, in regard to temperature, for these carbon electrodes, and the curves obtained on petroleum coke carbons made here in this laboratory.

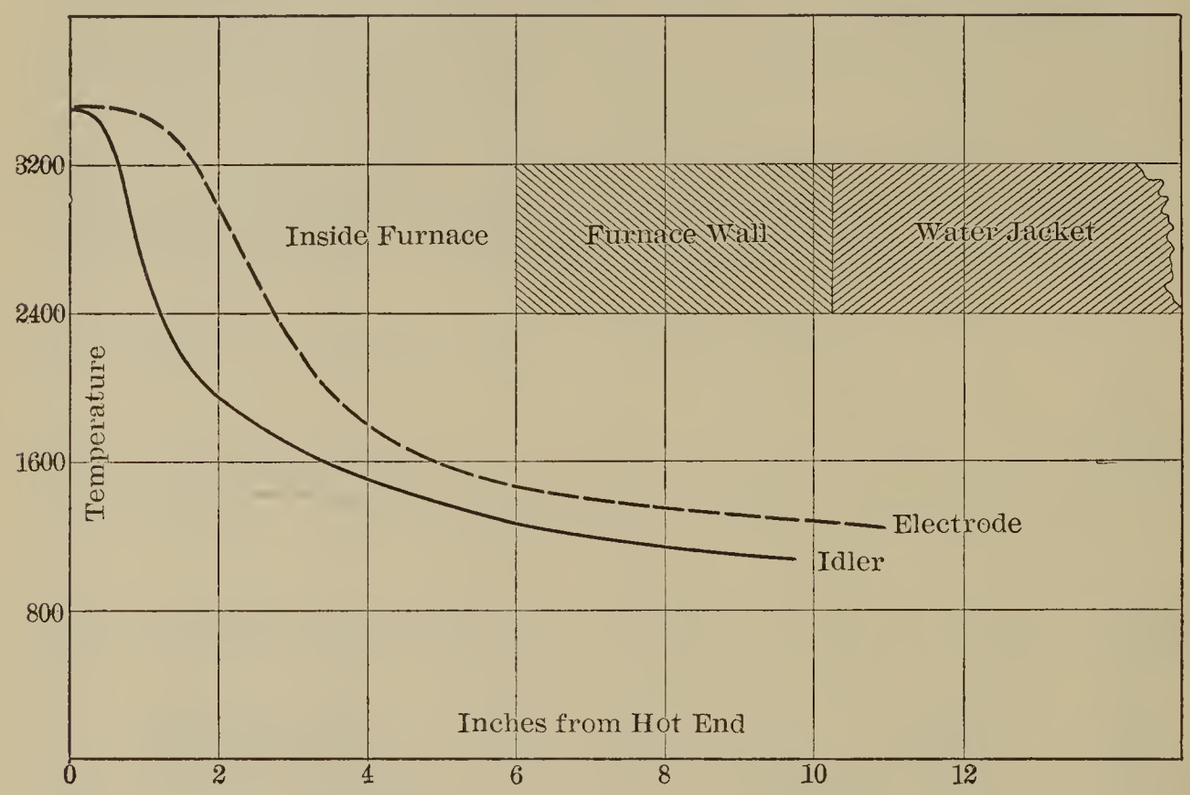


FIG. 8.

IDLER CARBON.

Section	A*	Resistance in Ohms / in³		Temperature C°
		Sample No. 1	Sample No. 2	
No. 1	0.25	0.000588	0.000640	3500 (Test Sample.)
No. 2	4.25	0.00210	0.00218	1540
No. 3	8.25	0.00245	0.00245	1240
No. 4	12.25	0.00252	0.00252	1080 (Orig. Fire Tem.)

*A = distance from hot end in inches to centre of sample, ½ inch thick.

A*	Absolute Density	Temperature Indicated	
¼	2.200	3500	(From Sample again.)
1¼	2.205	3500	
2¼	2.190	1900	
3¼	2.138	1640	
4¼	2.105	1500	
6½	2.105	1500	
8	2.048	1230	
12	2.015	1080	

*A = distance to centre of sample, ¼ inch thick.

On the hardness curve for the idler carbon, we have also three points which I think I may pick out. First, at 9″ back from the hot end, the curve becomes horizontal, showing that here we had reached the original firing temperature, which by absolute density was 1,080°. Second, the temperature at which maximum hardness is obtained is usually about 1,300°, here 5½″ back from hot end, and thirdly, the hardness curves usually change slope markedly at about 2,200°, which in this case is at a point 1½″ back from the hot end. The following temperature data may now be collected:

	Temperature by		
(A)	Abs. density	Resistance	Hardness
.25	3500	3500	
1.25	3500 (?)		
1.50			2200
2.25	1900		
3.25	1640		
4.25	1500	1540	
5.50			1300
6.50	1500 (?)		
8.0	1230		
8.25		1240	
9.			1080
12.	1080	1080	(original firing temperature).

(A), as usual, is the distance from the hot end of the idler to the point at which temperature is indicated.

With the exception of the two absolute density determinations followed by an interrogation point, the results are in good agreement. With reference to the first, or 3,500° point, it must again be said that the change of density between 2,000° and 3,500° is so slight that a small error in measurement can make a large temperature error. With reference to the second, or 1,500° point, the change in density is great enough so that 20° difference in temperature can easily be measured in this way, but the value is unaccountably off. This particular sample was lost, so that the determination could not be checked.

Plotting the collected temperature data, we get the temperature gradient which existed finally in the carbon idler, Fig. 7. Interpreting the other data at hand, by means of this temperature scale, we obtain the following curves:

Comparative temperature gradients for carbon idler and electrode, Fig. 8.

Hardness against firing temperature, Fig. 9.

Absolute density against firing temperature, Fig. 10[3].

Cold resistance against firing temperature, Fig. 11.

The curves are at least characteristic of the changes of petroleum coke carbon with firing temperature.

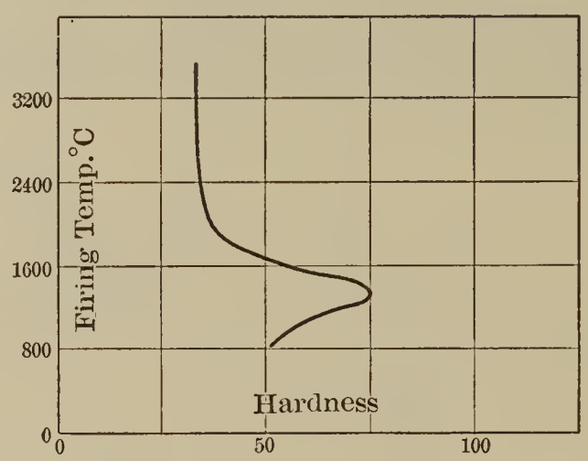


FIG. 9.

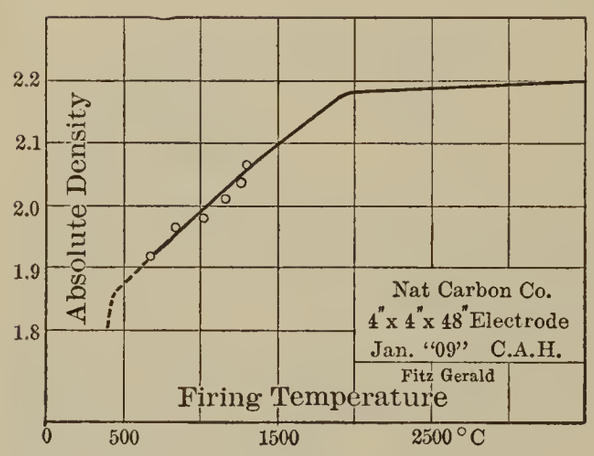


FIG. 10.

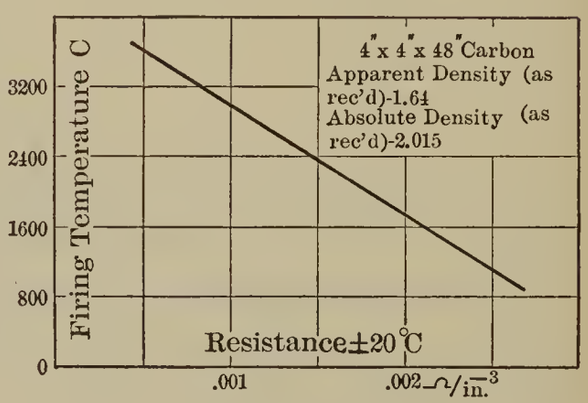


FIG. 11.

[3] I have taken the liberty of plotting absolute densities given by FitzGerald for petroleum coke carbons (Electrochem. Ind., Vol. II, p. 415) on the absolute density sheet, Fig. 10. The values were given as follows:

Absolute Density.	Temperature (FitzGerald).	Temperature (Hansen).
1.9141	dull red	650°
1.9612	above M. P. $CaCl_2$	850°
	below M. P. Ag.	
1.9853	above M. P. Ag	1000°
2.0061	above M. P. Cu	
	below M. P. cast iron	1150°
2.0363	above M. P. cast iron	1250°
2.0585	platinum crucible blast lamp	1300°

I assigned the temperature given numerically as representing FitzGerald's conditions, and simply plotted his densities on my curve. It is evident that temperatures obtained from my curve by applying FitzGerald's absolute densities could be reasonably assigned.

These curves bring out clearly, I think, the fact that the electrodes were graphitized at the tips in the course of the run and that the change from the amorphous stage to the graphite stage, if I may so call it, is a gradual one.

Conclusion.

While the experiments detailed are very crude, I think I have shown that for electrodes in furnaces of the type discussed, carbon electrodes are less wasteful of heat than graphite electrodes of the same cross section at current densities below 200 amperes per square inch. Varying the length of electrode may, to some extent, vary this critical current density.

I have shown that in furnaces taking 500 kw., the electrode losses can easily reach 15 per cent. of the total load impressed. Since the electrode losses are to a certain extent independent of the length of the furnace, if we shorten the furnace we increase the electrode loss to any amount above 15 per cent.

It also seems more reasonable to assign a ratio of the heat conductivities of graphite and carbon of about 8 to 1 under the conditions described. The ratio is brought down to this value from 18 to 1, probably owing to the partial graphitization of the carbon, and the ratio may vary somewhat with length of electrode for this reason.

APPENDIX.

Notes on Carbon.

In presenting the paper on "Electrode Losses," I used several lantern slides showing the changes in physical properties of various carbons with firing temperature, as well as a slide showing the resistance temperature diagram of various graphitized carbons. Several requests that they be published have come in to me, and I have sent in these prints for reproduction.

Lack of time prevents the writing at present of any extended article covering the results, but those interested can, of course, get the kernel of the nut from the curve sheets. The three carbons discussed were chosen from a large mass of similar data,

for the reason that they are typical of three rather distinct classes of carbon, and most carbons used in commercial practice will come under one or the other of them.

These curves will be raised or lowered bodily on the sheets as the proportion of binder (pitch) is increased or decreased, but the shape of the various curves will not be materially altered. In all cases here discussed the volume percentage of pitch was 41.3 per cent. of the total. The carbons were all made after a

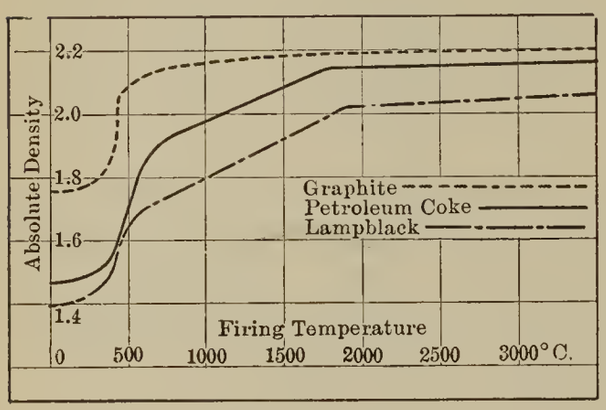


FIG. 12.

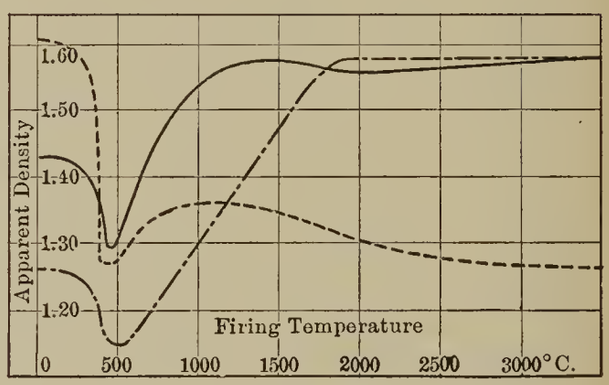


FIG. 13.

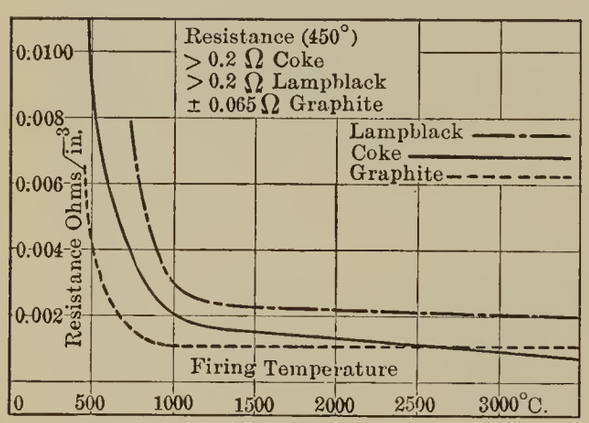


FIG. 14.

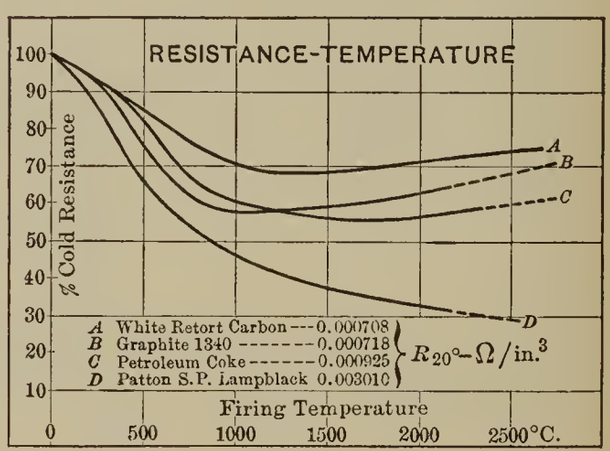


FIG. 15.

considerable experience with the manufacture of carbons and were mechanically flawless, *i. e.*, without the so-called "baking" or "shrinkage" cracks, without laminated structure, etc., and the materials used would all pass 150-mesh screen. The results here given can, by actual observation, be reproduced at will on new carbon batches. Further than to give the methods of measurement I do not care to go at present, but hope to have an article on carbon ready for publication within a short time.

Methods Used in Making Measurements.

Shrinkage. Average of shrinkage in three dimensions by Vernier Caliper.

Loss in Weight. Weight before and after firing.

Apparent Density. Vernier Caliper on rectangular samples and weights.

Absolute Density. This method was designed to facilitate a very large number of measurements per day, with comparatively little apparatus conveniently at hand for making them. The measurements are all strictly comparable among themselves, and are reproducible with a remarkable degree of accuracy. Small rods of carbon, approximately 3/8 inch diameter by 1 inch long, were cut out, dried, numbered or otherwise indexed with a knife, and weighed. They were then thrown into a benzole reservoir, 50 or 60 at a time, boiled for ten minutes, and then allowed to stand over night in benzole.[1] Samples were then transferred, one at a time, to a small, ground-glass stoppered pycnometer, with the ordinary vent in the top, and weighed in benzole. Benzole is the best penetrant for this work that I have found, and, unlike kerosene, which is often used, it does not change in density when a portion is boiled off. It has a very high temperature expansion coefficient and a very low heat capacity, however, and care must be taken in securing and keeping a uniform temperature or in correcting for measured temperature changes. From my own experience, there is far less liability to error with this method than when very fine powders are used, and better comparative results are obtained. Whether or not the densities are "absolute," I cannot say.

Resistance.

Resistance is measured by CR drop method, using a 1,500 ohm reflecting galvanometer, which is frequently calibrated against a standard voltmeter. Great care must be exercised in making the current connections, to secure uniform current distribution throughout the section of the sample, and the samples are used. Copper gauze between the sample and the spring

[1] Highly graphitic carbons are very much less readily impregnated with benzole than others, but even these reach constant weight in much less time than is allowed under the conditions cited.

clamp connection has been found very effective. A high resistance voltmeter or galvanometer is absolutely essential to reliable results. The results obtained above have been found to agree very closely with potentiometer measurements—as a rule they are 2 or 3 per cent. low. An 180-ohm millivoltmeter, used instead of the 1,500-ohm instrument, gave results that were often 50 per cent. low and in general 25 per cent. low under the same conditions.

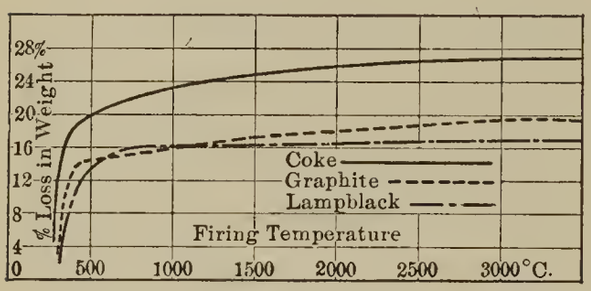


FIG. 16.

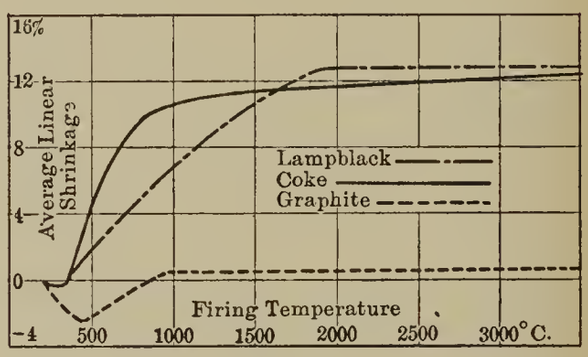


FIG. 17.

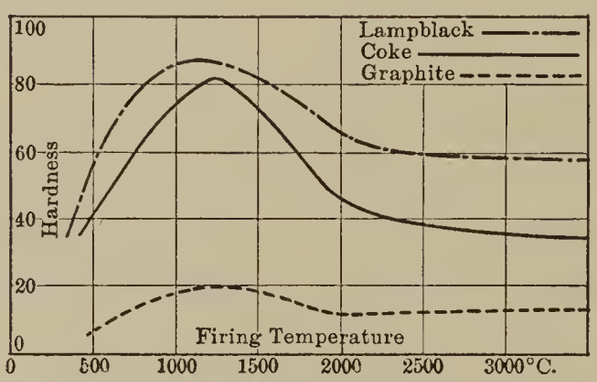


FIG. 18

HARDNESS.

This was made with a Shore scleroscope, using the diamond-pointed hammer. It places samples in the same order as a "scratch" test.

RESISTANCE TEMPERATURE.

The measurement of the resistance temperature coefficient of carbon offers a great many very serious experimental difficulties. The method chosen offers, in my opinion, less than most of those available, if properly worked out. Dr. G. K. Burgess some time ago estimated that a carbon incandescent lamp, running at 3.5 watts per candle, operated at 1,850° C. A large number of

determinations of the number of watts consumed per square inch of surface exposed at 3.5 watts per candle gives 410 as an average. The number of watts consumed per square inch of surface bears a perfectly definite ratio to the temperature of the surface: $E = KT_4$ when radiation only is considered, and this condition is closely approximated both in the incandescent lamp and in the experiments which follow. Carbon rods were heated, by passing current through them, in a container exhausted to a pressure comparable with that of the incandescent lamp. Resistance was measured by CR drop method and temperature was estimated from the number of watts per square inch of surface exposed. The resistance temperature coefficient of a carbon varies to a remarkable degree with apparent density, fineness of the carbon flour, and with the method of manufacture. This is, however, altogether too big a subject to treat as a postscript.

Research Laboratory,
General Electric Company,
February 1, 1909.

DISCUSSION.

MR. F. A. LIDBURY: I wish firstly to congratulate Mr. Hansen on having attacked in a very ingenious and satisfactory manner a problem of great importance to all users of electric furnaces. In particular, the data accumulated upon the physical properties of carbon with reference to their change with temperature will be extremely useful in further investigations along similar lines.

At the same time, I think it is rather unfortunate that Mr. Hansen did not state more explicitly (though possibly it is sufficiently obvious) that the conclusions to be drawn from his experiments are applicable only to one particular type of electrodes, namely, the short water-cooled electrode of which the only portion projecting from the furnace is the water-cooled head. The results obtained by Mr. Hansen probably represent as near an approach to ideal scientific measurements as can possibly be obtained in such cases, and clearly show that *under the conditions*

referred to the additional loss down the graphite electrode, though its high thermal conductivity forms a very important factor, and outweighs the advantages which this electrode possesses in virtue of its lower C_2R losses. But it must not be overlooked—and this is the point I rose to make—that the electrodes with which Mr. Hansen worked are precisely of that type in which heat-conductance losses have their maximum and C_2R losses their minimum effect, and that in electrodes of greater length in relation to cross-section, and particularly if the temperature gradient is lower owing to absence of water-cooled heads, the C_2R losses become of greater significance, and the heat-conductance losses of less.

Mr. Carl Hering: I am very much interested in this subject, and I congratulate Mr. Hansen on his very interesting paper, which will aid us greatly in designing furnaces. I would liked to have said quite a little on this subject, as I have given it considerable attention, but the time is so short that I will confine myself to a few points.

One of them is this: I have long held that it ought to be possible in some way to have these two losses (namely the C_2R loss and the heat conduction loss) co-operate to produce a minimum. It seems to me that this could be done in the following way: Suppose the electrode to be so proportioned that very near the hot end it becomes heated by the current to a slightly higher temperature than that of the furnace, even if it is only a degree or a fraction of a degree. The heat gradient from this point will then *fall* toward the furnace end; hence, a slight amount of heat will then flow that way, namely, into the furnace, and it will therefore be impossible for any furnace heat to flow out through that electrode to the outside of the furnace, because heat cannot flow in both directions through the same section at the same time. In other words, it will thus become possible to make the C_2R heat act as a check valve, so to speak, to allow the current to flow into the furnace, but not allow any of the furnace heat to flow back.

Whether practical considerations will permit these conditions to be reached is a question for the designer to decide in each particular case. It is well, however, to know that such a possi-

bility exists, as we then at least know in what direction to go, and can approach it as closely as circumstances permit.

There is one other point: I have not yet completed my investigation, but I can at least say now that in general it is true that for the same cross-section of electrode, the heat conduction losses diminish as the length increases, hence the curve representing these losses as ordinates is a falling curve; the C_2R loss, on the other hand, increases as the electrode becomes longer, hence its curve is a rising one. But the sum of the ordinates of two such curves is always a curve having a minimum point; this means that for some length the combined losses are least, if the total loss is really the sum of the two. In this way it will be found that for different cross-sections and lengths these minima are all the same in amount, that is, this minimum cannot be made smaller by changes of dimensions. This seems rather surprising and interesting. I will have more to say about this as soon as I get the results into better shape.

Prof. J. W. Richards: Mr. Hering's remark about keeping the temperature of the electrode just outside of the inside wall of the furnace a little higher than the temperature just inside, reminds me of the picture which used to amuse me very much when I was a little boy, of a man seated on a donkey and holding a carrot a little ahead of the donkey's nose in order to get more speed out of him. (Laughter.)

Mr. Hering: Well, it worked all right, did it not?

Prof. Richards: It did. (Renewed laughter.)

Mr. Hering: Then by analogy, at least, my method ought to work that way also.

Referring to another point in Mr. Hansen's paper, I do not think that the comparative test illustrated in Fig. 4 is quite fair to the graphite electrodes, because they are there made the same size as the carbons. I think the sizes ought to have been taken in proportion to their conductivities to get fairer results.

Mr. A. M. Williamson: I noticed, Mr. Chairman, in reading the advance copy of this paper, that the specific resistance of graphite given is very high, in fact, about twice the actual figures. The point of this is that Mr. Hansen in taking carbon electrodes

as having four times the resistance of the graphite as given, arrived at a result he could not explain. I think that if he takes the correct figures for both carbon and graphite, the results obtained will be more easy of explanation.

MR. HERING: I think the remark I made about the possible method of stopping the overflow of furnace heat through the electrodes explains the result which Mr. Hansen says, in his paper, he sees no reasonable explanation of; this result was that the heat which escaped at the cold end was less than the C_2R loss in the electrode.

MR. HANSEN: I think I made that point definitely, Mr. Chairman, that the heat probably flowed both ways.

A paper presented at the Fifteenth General Meeting of the American Electrochemical Society, at Niagara Falls, Canada, May 7, 1909; President E. G. Acheson in the Chair.

A NEW TYPE OF AMMETER FOR THE ACCURATE MEASUREMENT OF ALTERNATING CURRENTS ABOVE 1000 AMPERES.

By Edwin F. Northrup, Ph. D.

The accurate measurement of alternating currents, too large to be measured by a Kelvin balance or a Siemens' type of electrodynamometer, has been hitherto a difficult and costly measurement seldom made. The usual practice has been to construct a series transformer which yields a small secondary current, which is easily measured by well-known methods, and to determine the large primary current from the calculated ratio of transformation of the transformer. The precision of a measurement so made can be no better than the accuracy with which it is possible to calculate the ratio of transformation of the transformer. As this ratio varies with the load, the frequency, the wave form of the current, the magnetic leakage, the eddy current losses and with other less important influences, the accuracy with which the calculation of the ratio can be made is very low. A simple and more precise method of measurement—one which may be used to experimentally find the ratio of a series transformer—is much to be desired.

The new method, here proposed, is based upon the utilization in a current meter, of the recently observed centripetal pressure which exists in the interior of a liquid conductor carrying an electric current. When an electric current of large density is passed through a fine jet or stream of mercury or molten metal, the stream suffers, at some point of its length, a constriction and, if the current is sufficient, the constriction divides the stream with consequent vaporization of the metal. This fact was observed and first described by Paul Bary, (L'Industrie Electrique, April 25, 1901, and later, August 25, 1902, June 10, 1903). In the summer of 1906, Mr. Carl Hering observed a manifestation of

the same force in a large resistance furnace in which a part of the circuit consisted of metal kept melted by the current. Acting upon this observation of Mr. Hering, the writer investigated experimentally and theoretically the nature of the phenomena and the forces producing them and presented his treatment of the matter at the New York meeting of the American Physical Society, March 2, 1907. This presentation, without alterations or additions, was published in the Physical Review, June, 1907, under the title "Some Newly Observed Manifestations of Forces in the Interior of an Electric Conductor." In the issue of L'Eclairage Electrique, April 13, 1907, Mr. Paul Bary gave practically the same explanation of the pressure forces in a conductor as was given by the writer in March. Mr. Bary's paper was entitled "Actions Mechaniques du Courant dans les Conducteurs Electriques." Mr. Hering put on record his original observations and explanation of the phenomenon as manifested in resistance furnaces in a paper read before the American Electrochemical Society, May 3, 1907, at Philadelphia, Pa. His paper was entitled "A Practical Limitation of Resistance Furnaces; the 'Pinch' Phenomenon." In the writer's paper, delivered March 2, 1907, an ammeter was described and shown working, which measured direct or alternating currents, its operation depending upon the pressure forces in a conductor. Later several other ammeters for the commercial measurement of large alternating currents were constructed. The success and accuracy of these instruments suggested that apparatus carefully constructed on similar principles might be used for accurately measuring a large electric current even, perhaps, in absolute measure. The following pages give an examination of the laws which govern the pressures in a conductor of circular cross section, a description of a commercial apparatus now fully developed, which is suitable for measuring large alternating currents with precision, and a proposed method for the absolute measurement of current.

Analytical Theory of the Ammeter.

In Fig. 1, B is a vertical section and A a cross section on the line ab of B. Hg is a cell filled with mercury. When an electric current passes from j to k through the mercury, a difference

of hydrostatic pressure is created between the outer and inner circumferences of the circular cell. In order to determine this pressure-difference a communication must be established between the outer and inner circumferences of the cell. This may be accomplished by the arrangement diagrammatically shown in the section B. When current flows, mercury will tend to flow down the tube p_1 and up the tube p_2. This flow will continue until the difference in level at which the mercury stands in the tubes p_1 and p_2 establishes a pressure-difference equal and opposite to that produced by the current between the inner and outer cir-

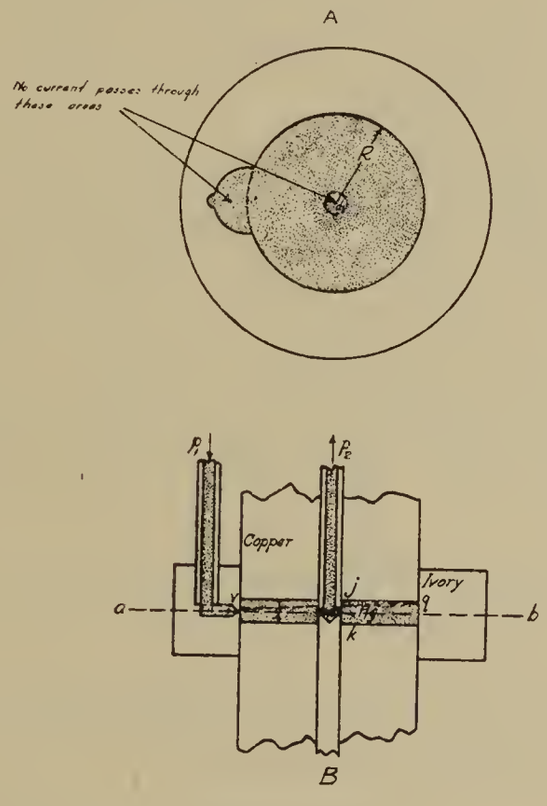


FIG. 1.

cumferences of the cell. By measuring the difference in level between the tubes p_2 and p_1 the pressure-difference produced by the current may be determined. If the conditions are rightly arranged, the current will be a known function of this pressure-difference and hence the current value may become known.

Inasmuch as the tube p_2, which communicates with the interior of the cell, must have a finite diameter, and as this tube consists of insulating material, such as ivory, which is necessitated by the condition for obtaining a uniform current distribution in the cell, it becomes necessary to determine the pressure-difference

between the inner and outer walls of the hollow liquid cylinder as a determinate function of the current which flows with uniform distribution throughout a right cross section of the cylinder. This, as will be shown, is a perfectly determinate problem, but one which involves certain assumptions if it is required to calculate the instrumental constant. These assumptions, however, may be realized in practice by employing properly constructed apparatus for the purpose. Of the assumptions made, three have especial importance:

The cross section is that of a circular cylinder having a common axis for its inner and outer circumferences.

The current distribution throughout a right section of the cylinder is perfectly uniform.

The lines of current flow in the cell or hollow cylinder are everywhere throughout its axial length parallel to the axis.

If it is desired to calculate the instrumental constant, which would be the case if the current to be measured is greater than could be obtained for calibration purposes, we must realize to the full the above assumptions and other less important ones. Certain conditions and a certain construction also must be observed.

The mercury cell is easily given the proper form and accurate dimensions by forming its circumferential surfaces of ivory turned out of solid blocks. This part of the construction has been successfully tried in several ammeters constructed for the commercial measurement of current.

The assumption of uniform current distribution requires the most care. As mercury has over 60 times the resistance of copper the current distribution throughout the mercury cell would not be uniform if the upper and lower faces of the cell were not parallel. Thus, if the upper face of the cell were inclined as indicated by the dotted line qv, the current density would be greater in the left-hand than in the right-hand half of the cell. Though the intensity of the pressure is independent of the axial length of the cell, it is nevertheless necessary to give the cell a moderate length so that the percentage difference between different parts of its faces, taken as parallel, may be small. To secure a justification of the assumption of uniform current distribution,

the construction of the cell in respect to the points above mentioned must be attended to with special care, if the instrumental constant is to be calculated.

The parallelism of the lines of current flow throughout all portions of the cell may be secured by the construction indicated in Fig. 1 B. Here the mercury enters the outer circumference of the cell through a narrow slit not over half a millimeter wide, and leaves the cell from the inner circumference, entering the tube p_2 through a similar narrow slit. With such narrow slits the lines of current flow cannot bend into the spaces where the mercury enters and leaves the cell.

The pressure-difference produced by the current might be determined by measuring directly the difference in level at which the mercury is caused to stand by the current in two tubes as p_1 and p_2, but a more accurate method is available.

The following calculations are based upon the methods described by the writer in the Physical Review, *24*, 474-497 (June, 1907.)

It is required to find, first, the hydrostatic pressure in the substance of a hollow cylinder at any point distant r from its axis, this pressure being produced by a current I flowing parallel to the axis of the cylinder. Let d = the radius of the internal wall and R = the radius of the external wall of the cylinder.

The intensity of the magnetic field at any point in the substance of the cylinder distant r from its axis is:

$$T = 2I \frac{r^2 - d^2}{(R^2 - d^2)\, r} \qquad (1)$$

(See Physical Review, June, 1907, p 479, eq. 3, or Maxwell, § 683, eq. 12.)

The area of the annular ring of radial depth dr and of inside radius r is:

$$da = 2 \pi \, rdr \qquad (2)$$

In the case of uniform current distribution throughout the cross section of the cylinder the ratio of the current carried by

the portion of the cylinder which has as its cross section the annular ring to the total current is:

$$\frac{di}{I} = \frac{2\pi\, rdr}{\pi\,(R^2 - d^2)}$$

Whence we obtain,

$$di = \frac{2\, I\, rdr}{R^2 - d^2} \qquad (3)$$

The force with which the element carrying the current, di, tends to move toward the axis of the cylinder is:

$$-dF = l\ di\ T \qquad (4)$$

where l is the length of the element considered.

If we call — dg the force per unit of area which acts radially inward, we have

$$-\frac{d\ F}{2\pi\, r\, l} = -dg = \frac{l\ di\ T}{2\pi\, r\, l} = \frac{di\ T}{2\pi\, r} \qquad (5)$$

Replacing in eq. (5) the value of T from eq. (1) and the value of di from eq. (3) we obtain,

$$-dg = \frac{2\, I^2}{\pi\,(R^2 - d^2)^2}\left(rdr - d^2\ \frac{dr}{r}\right) \qquad (6)$$

Since the pressure-difference which is to be measured is exerted between the outer and inner circumferences of the cylinder, we have to integrate eq. (6) between the limits R and d. Note that the negative sign before dg indicates that the pressure decreases in the direction in which r is taken to increase. Indicating the integration of eq. (6) and calling P the resulting pressure-difference, we have

$$P = \frac{2\, I^2}{\pi\,(R^2 - d^2)^2}\left(\int_d^R rdr - d^2 \int_d^R \frac{dr}{r}\right) \qquad (7)$$

From eq. (7) we obtain

$$P = \frac{I^2}{\pi\,(R^2 - d^2)}\left(1 + \frac{2\, d^2}{R^2 - d^2}\log_e \frac{d}{R}\right) \qquad (8)$$

Solving for the current we have,

$$I = \sqrt{P}\,\sqrt{\frac{\pi\,(R^2 - d^2)}{1 + \frac{2\,d^2}{R^2 - d^2}\log_e \frac{d}{R}}} \qquad (9)$$

Assuming that $d = o$ we have

$$I' = R\sqrt{\pi P} \qquad (10)$$

Here P is the intensity of a force and its dimensions are $L^{-1}M.T^{-2}$ and R is a length. Hence the dimensions of the current by eq. (10) are, correctly, $L^{\frac{1}{2}}\,M^{\frac{1}{2}}\,T^{-1}$.

The quantity,

$$\sqrt{\frac{\pi\,(R^2 - d^2)}{1 + \frac{2\,d^2}{R^2 - d^2}\log_e \frac{d}{R}}}$$

is a constant, on the assumption of uniform current distribution, and depends only upon the geometrical dimensions given to the cell of the current meter. If we call this constant $\triangle$ then,

$$I = \triangle\sqrt{P} \qquad (11)$$

The assumption of uniform current distribution is entirely justified for the case of direct and slowly alternating currents and is so practically for frequencies as great as 133 cycles per second. Owing to the so-called "skin effect," with rapidly alternating currents, the current tends to leave the center of the cell and to crowd toward the circumference. We shall examine later the error which might arise from this cause, if the calculation is based upon the assumption of uniform distribution, and we shall find that it is negligibly small.

The constant $\triangle$ can be determined, of course, experimentally with very high precision by using a direct current, which is measured with a potentiometer, and by determining at the same time the pressure P.

If a meter, however, is to measure several thousand amperes, the outfit for making an experimental determination of the constant $\triangle$ would be elaborate and costly, and it is very desirable, therefore, to know all the conditions of the problem and be able

to determine Δ by calculation. Even if Δ is to be verified afterwards by experiment, it is desirable to be able to calculate its value so that the performance of a particular meter may be predetermined from its design.

Cells in Series.

While to measure the current it is necessary only to determine the pressure difference between the center and the circumference of a single cell of mercury, there are reasons, based upon simplicity of construction and increased accuracy, why it is often desirable to pass the current through several mercury cells in series and arrange the construction so that the pressure-differences set up in all the cells are added together.

The pressure-differences in a number of cells are so added together, when the center of one cell is joined with one or more small tubes to the circumference of the next, the center of that one to the circumference of the next one, and so on throughout the series. The manner in which this is carried out in practice is shown plainly by the cross sectioned view of the 2,000-ampere meter illustrated in Fig. 3. When the pressure-differences of n equal cells are added thus in series, the final pressure is n times as great as that of one cell. Formula (8) will then become:

$$p = \frac{n\, I^2}{\pi\,(R^2 - d^2)} \left(1 + \frac{2\, d^2}{R^2 - d^2} \log_e \frac{d}{R}\right) \qquad (12)$$

or

$$I = \sqrt{\frac{p}{n}} \sqrt{\frac{\pi\,(R^2 - d^2)}{1 + \frac{2\, d^2}{R^2 - d^2} \log_e \frac{d}{R}}} \qquad (13)$$

We wish now to determine the power which is dissipated in the cells of a multicellular meter.

Let $d = o$, then eq. (13) becomes,

$$I^2 = \frac{p\, A}{n} \qquad (14)$$

where A is the area of one cell. The power dissipated in one cell will be $w = I^2 r$, where r is the ohmic resistance of the cell.

If l is the axial length of the cell and ρ is the specific resistance of mercury, we have $r = \frac{\rho\ l}{A}$ Hence, if W = n.w is the total power dissipated in the meter, we have,

$$W = \frac{n\ I^2\ \rho\ l}{A} \qquad (15)$$

Or using the value of I^2 of (14) in (15) we have,

$$W = p\ \rho\ l \qquad (16)$$

Eq. (16) leads to the important conclusions that the power which will be dissipated in any construction of mercury ammeter of the type above described is independent of the number of cells used and of the area of these cells, but is numerically equal to the pressure produced, to the specific resistance of the liquid in the cells, and to the axial length of each cell. It follows, using cells of a fixed axial length and mercury as the working liquid, that the watts which must be expended to produce unit of pressure is a fixed quantity.

Suppose it is required to produce a pressure which will raise a column of water 50 cms. and suppose the axial length of the cell or cells is 0.05 cm., then however we vary the number of cells and their area, the watts which will be dissipated is a fixed quantity and may be calculated as follows:

In equation (16) express all the quantities in c. g. s. units. We shall then have, p = 50 x 981 dynes, because a force which will sustain a column of water with a cross section of 1 square cm. is a measure of hydrostatic pressure, and a column of water of this cross section and 50 centimeters high will weigh 50 grams or produce a pressure at its base of 50 x 981 dynes.

$$\rho = \frac{10^{-4}}{1.063} \text{ ohms.}$$

Or, as 1 ohm is 10^9 c. g. s. units,

$$\rho = \frac{10^5}{1.063} \text{ c. g. s. units.}$$

Since l = 0.05 cm. and 1 watt = 10^7 c. g. s. units, we have finally,

$$W_1 = \frac{50 \times 981 \times 10^5 \times .05}{1.063 \times 10^7} = 23. + \text{ watts.}$$

This last result shows, that if the meter is constructed to raise a column of water, as an index of the pressure produced by the current, and if the axial length of the cell or cells is 1/2 m/m (which is a length that is practical to employ), and mercury is used as the fluid in the cells, then there will be expended in the meter approximately one watt for every two centimeters to which the column of water is raised.

It is evident from this that if it is required to have the scale of the meter 50 cms. high, it must be able to get rid of the heat produced by 23 watts, and this follows entirely regardless of the current which is measured. The surface for getting rid of heat for a meter with a scale 50 cms. high must be as great for a 200 ampere instrument as for one built for 10,000 amperes. The above reasoning assumes that the heat which is developed in the parts of the meter which are made of copper may be neglected as being very small when compared with that developed in the mercury. The following comparison may be made here. If a direct current of 2,000 amperes is measured by reading with a millivoltmeter a drop of 150 millivolts over a shunt, the power dissipated in the shunt is 300 watts. The power thus wasted is over ten times the power consumed in the mercury meter when reading at a scale height of 50 cms.

From the above considerations, it would seem that there is nothing to gain by designing the meter to have more than one cell. Experience shows, however, that several minor advantages are gained by using two or more cells. Since the pressure with a given current is proportional to the number of cells divided by the area of one cell, it follows that as the number of cells is increased, the current density in any one cell is diminished. The heat developed, therefore, is less localized with several cells. Also, if several cells are used, the area of each is larger, and hence their exact dimensions are more easily determined. Further, if only one cell is used its area would be small for small current meters, and any cause, as a spot of poor amalgamation of the surface of the cell, tending to disturb the uniform current density in the cell has a relatively larger percentage influence than is the case where several cells of larger area are used.

Also, the mechanical construction, as illustrated in Fig. 3,

lends itself very suitably to two, four, six or eight cells, etc., and the commercial form of the meter is made with two or a greater even number of cells. The smaller the current which is to be measured, the smaller must be the area of any one cell, and the greater is the number of cells which it is desirable to use. The terminals of a small current meter may be smaller, but the greater number of cells which it is desirable to employ makes the cost of construction not far different for a small than for a large current instrument. Where a 50 cm. scale is to be used, the instrument is hardly adapted to the accurate measurement of currents under 200 to 500 amperes at full scale reading.

Its field of special usefulness is to be found in the accurate measurement of alternating currents of over 1,000 amperes, there being no assignable upper limit to the current which may be measured.

Methods of Measuring the Pressure.

If one tube communicates with the circumference and one with the center of a mercury cell, and mercury stands at the same level in these two tubes when no current is flowing through the meter, then, as soon as current flows, the mercury level will fall in the first tube and rise in the second. The difference in level produced is independent of the shape and diameter of the two tubes, but is directly dependent upon the square of the current which flows, and, for the reasons given above, the difference in level of mercury which can be obtained is approximately 1.6 mm. per watt of power expended in the meter. The difference in level of two mercury columns might be read directly with a cathetometer, but to make the instrument a practical ammeter which will read the value of the current on a long scale, laid off in amperes, it is necessary to greatly magnify the small motion that mercury would have. This might be done by causing the rising column of mercury to move a pointer, with a multiplied motion, over a straight or circular scale. It has seemed a better plan, however, to use a column of colored water as the indicator.

The manner in which water is made to serve as an indicator, the column rising approximately thirteen times as high as a mercury column, is shown plainly in Fig. 3. The mercury well,

which communicates with the center of a cell, is given a large diameter and the surface of the mercury in this well only rises a fraction of a millimeter when the water column rises 50 or more cm. With this construction, the friction which the surface line of the mercury makes with the wall of the well is vanishingly small and has no influence on the precision of the indications or on the accurate return to zero of the water column when the current is turned off.

Water, colored red, is used as the indicator in preference to all other liquids on account of its small coefficient of expansion at room temperatures. Water at 20° C. expands 0.02 per cent. per degree C., while kerosene oil, which was used in earlier instruments, expands 0.10 per cent. per degree C.

The water is kept from evaporating by joining with a small metal tube the top of the glass tube in which it rises to the top of another well in communication with the circumference of a cell.

The height to which the water column will rise with a given current passed through a meter having known dimensions may be calculated, or, if large direct currents are available for the purpose, the constant of the instrument may be determined experimentally for a single value of the current. As the instrument obeys the square law, the other marks on the scale may be laid off by calculation.

Mechanical Constructions.

The greatest difficulties encountered in the development of the meter up to the point where it might be considered commercially practical were found in the working out and the testing of structural details. Not less than eight radically different forms of construction were designed and tested before the form here described was reached and found to be fully satisfactory. Though each form of construction tried developed points of scientific and commercial interest, space will only permit me to describe briefly the latest form into which the instrument has crystallized. This present form is intended to serve as a laboratory and calibrating instrument, and for use in measuring large currents in connection with electric welding and electric furnace

practice. Non-essential modifications would fit the meter for use on alternating or direct current switchboards, but no designs having this use in view have as yet been worked out. The

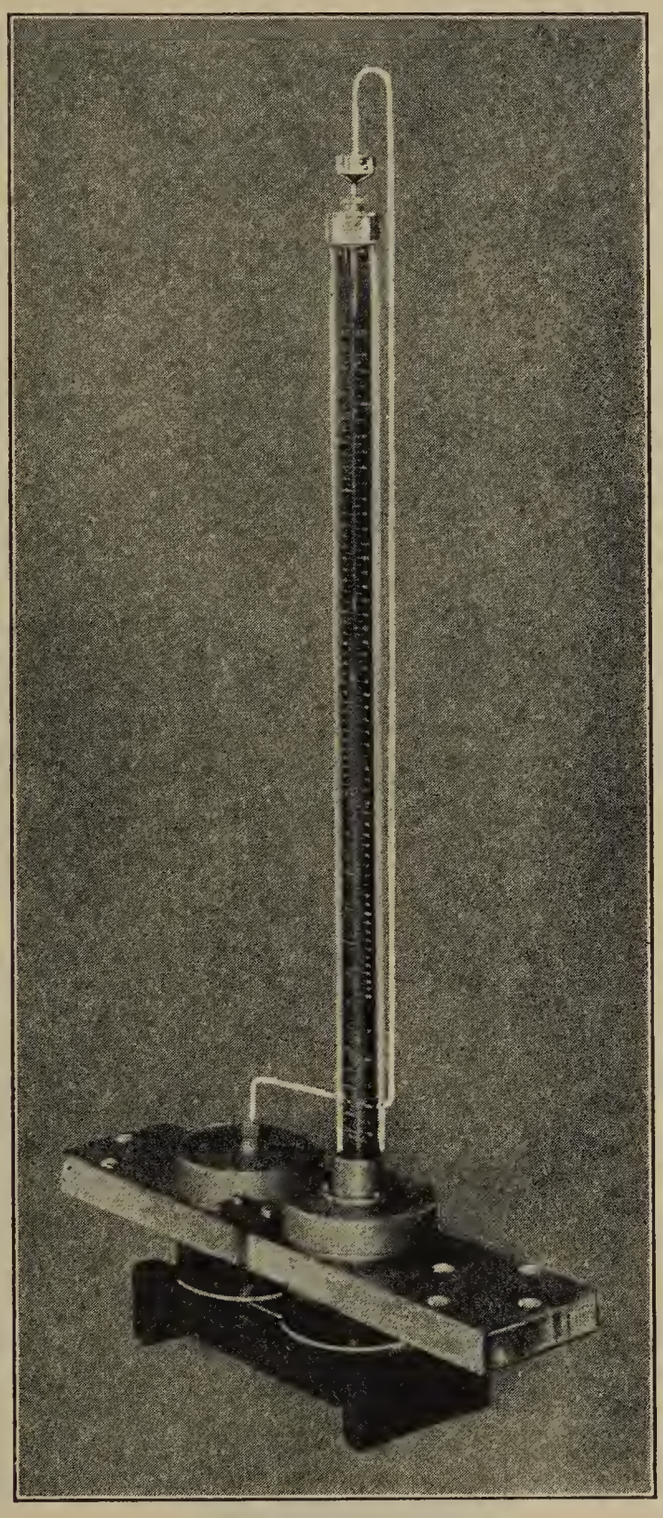


FIG. 2.

description given applies to a meter which reads 2,000 amperes at about the 50 cm. mark on the scale. The constant of the instru-

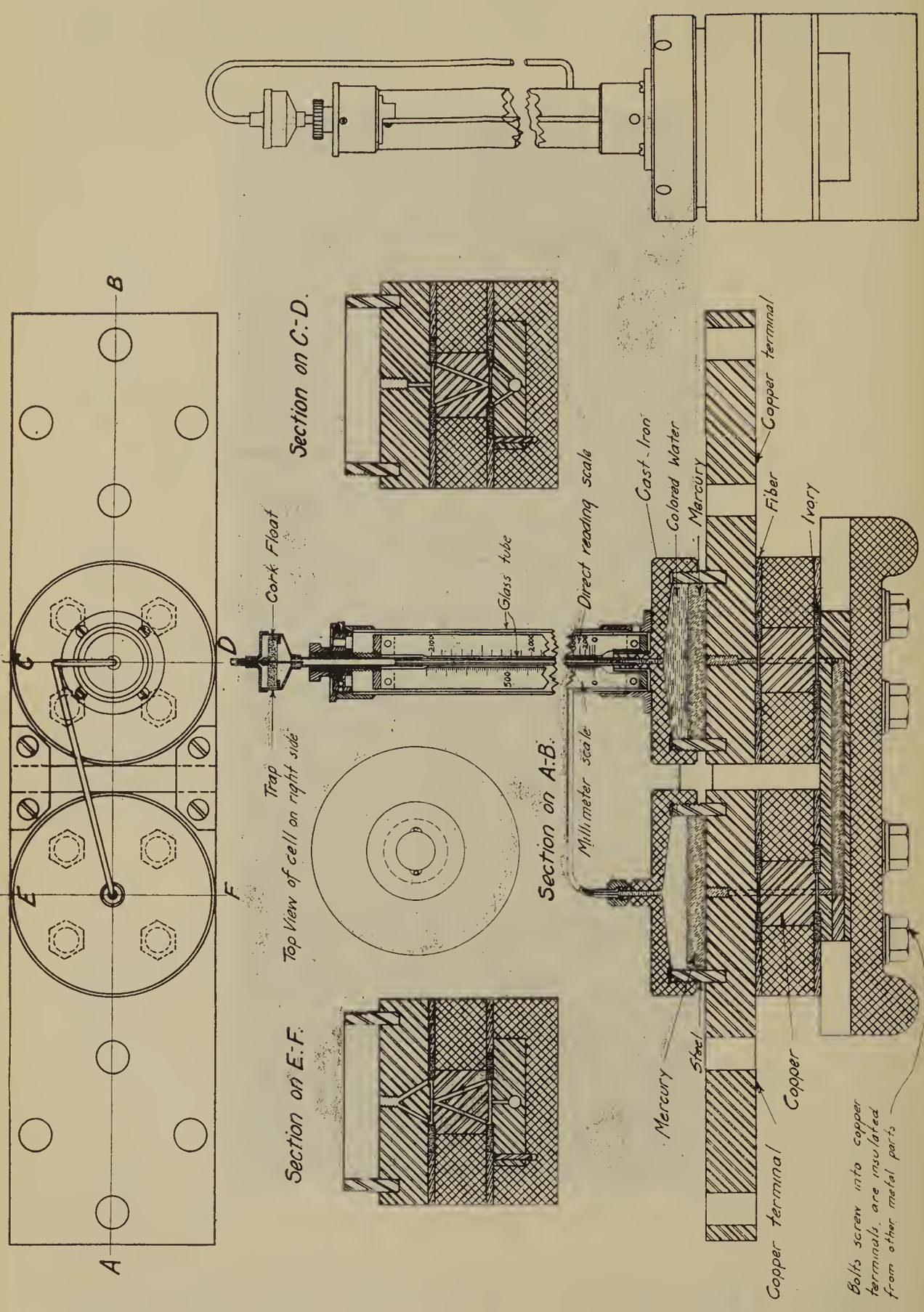

A
B
C
D
E
F
Cork Float
Trap
Top View of cell on right side
Section on C-D.
Section on E-F.
Glass tube
Direct reading scale
Millimeter scale
Section on A-B.
Cast-Iron
Colored Water
Mercury
Fiber
Ivory
Copper terminal
Mercury
Steel
Copper
Copper terminal
Bolts screw into copper terminals, are insulated from other metal parts

FIG. 3.

ment is easily changed, so that it will read from 500, say, to 6,000 amperes at the same scale mark by simply changing the area of its four mercury cells. The only variation, within these wide limits, in the cost of construction would come from the increased cost of experimentally determining the constant of a meter of the larger current capacity.

Fig. 2 gives an electrotype view of a 2,000 ampere meter, and Fig. 3 is a drawing which shows a top view, an end view, a section on the line AB, and sections on the lines ef and cd.

The markings on the drawing make a description of details unnecessary.

One important feature deserves, however, especial mention. It will be noted that the two holes which join the circumference of one cell to the center of the next cell enter the circumference of a cell on that diameter of the cell which lies at right angles to the

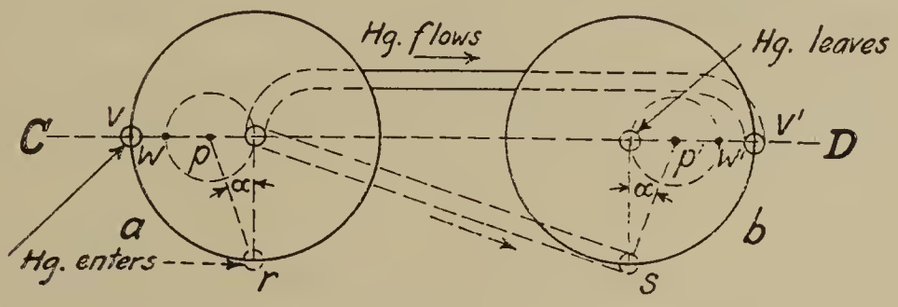


FIG. 4.

plane through the centers of the set of cells on the right and left. This point being neglected in the earlier constructions, it was found that the meter did not exactly obey the "square" law. The cause of the variation was finally located, and may be explained with the aid of the diagram, Fig. 4.

Let a represent a top view of the cell on the left and b of the cell on the right. Suppose the circumferential and center holes lie on the line CD. Assume that current flows downward perpendicularly to the plane of the cell through the cell a, and upward through the cell b. Then, owing to the repulsive force which the currents in a and b will exert upon each other, the centers of maximum pressure will be driven in the cell a to some point p to the left of the center hole and in the cell b to some point p′ to the right of the center hole. As a result of this, the pressure difference in cell a which will be utilized will be that which exists

between the two points w and v, instead of between the center and v, and in cell b between the points w′ and v′. The greater the downward current in a, and the upward current in b, the greater will be this shifting of the centers of maximum pressure to the left and to the right of the geometrical centers of the cells, and, with increasing current, the meter will read lower than it should read if it strictly obeyed the square law. Suppose now, however, that the mercury enters the circumference of the cell a at the point r, and the cell b at the point s, then the pressure difference which cell a would exert would be the difference in pressure between the points r and the geometrical center, which is very little different from that between the points r and p. Likewise with cell b, the maximum difference in pressure lies at the extremities of the line s and p′, while the pressure-difference which is measured lies at the extremities of the line which connects s and the geometrical center. In other words, of the maximum pressure-difference P, which should be measured, only the portion $P\cos\alpha$ is actually measured. With a wrong construction, errors from this cause as great as four to five per cent. may be produced, but with a correct construction, the errors are too small to be detected.

The axial depth of each of the four cells is made only 0.5 mm., which was found to be quite sufficient to permit the mercury to flow with perfect freedom between the well amalgamated faces of the cells. Carefully turned rings of ivory quite effectively maintain unchanged the separation of the opposing faces of the cells, and absolutely prevent permanently any leakage of the mercury.

For instruments which are to have their constants determined experimentally and not by calculation it was found not to be necessary to line with insulating material the walls of the tubes connecting the centers to the circumferences of the cells. If the fluid used in the cells had the same resistivity as copper, then unless the connecting tubes had an insulating lining, there would be a back pressure produced in the tubes themselves which would exactly neutralize the pressure-difference between center and circumference of the cells, and no resultant pressure-difference would be shown. But as mercury has 60 times the resistivity of

copper, very little current flows through the mercury in the tubes, and the back pressure set up in the tubes is too small to consider.

Since the rise in the column of water is proportional to the square of the current, a very little overload of current would cause the water to rise to the top of the tube and to descend through the tube connecting the index tube with the well on the left. If this accident were to occur, it would be necessary to remove the caps and refill with water the cell on the right. To avoid this possibility, a trap is provided at the top of the scale, which stops the rise of water at the top of the tube. Its simple construction is made apparent by an inspection of the diagram, Fig. 3.

The scale consists of two brass strips which lie on the right and left of the index tube. On the right hand strip, a scale reading in amperes is laid off, and on the left hand strip is marked a millimeter scale. This last may be used with a knowledge of the constant of the instrument, when one wishes to read to a high precision. The scale is made 50 cm. high, but the size and heat dissipating power of the meter is such, that, if demanded, the scale could be a meter or more high. An external glass tube protects the internal index tube and brass scale. This latter may be rotated for convenience of reading from any point of view.

When full current is suddenly turned on, the red liquid column rises from zero to full scale reading in from 4 to 5 seconds, and returns very exactly to zero in the same time when the current is turned off. The movement of the fluid column is just short of aperiodic, and follows every fluctuation of the current with great sensitiveness. It is an instrument which is very comforting to read after one has worked with a Kelvin balance which persists, with fluctuating currents, in perpetually oscillating.

The scale has a vertical adjustment sufficient to take care of changes in the zero which will result from tipping the instrument. If the zero is set when the instrument is cold, and it is afterwards used until warm, there will be a rise of about one millimeter in the zero; but when the scale is reset, the accuracy of the indications is restored, having a very small error resulting from a change in the density of the water.

Accuracy and Sources of Error.

The precision with which measurements of direct and alternating currents may be made with the mercury meter was very carefully determined by a series of measurements made at the Electrical Testing Laboratories in New York. The tests were made upon a meter with a capacity of a little over 2,000 amperes. The figures of chief interest obtained in these tests are given below, just as they were observed.

Test for Friction or Lag.

A potentiometer and shunt were used in this test to measure the true value of the direct current employed.

The readings of the height of the water column of the mercury meter were made on a millimeter scale ruled on brass. The column of water was raised to a particular mark upon the scale by increasing the current, and when the meniscus of the rising water column reached the mark the current was read with the potentiometer. The column was then lowered by decreasing the current from a higher value to the same mark and the current again read. A characteristic set of readings are given below:

Room Temperature at Start = 16° Centigrade.
Instrument Temperature at Start = 16° Centigrade.

Liquid	Mm. Mark on Scale	True Value of Current in Amperes	Temperature of Instrument
Rising	500	2023.0	19°C.
Falling	500	2023.2	20°C.
Rising	500	2023.0	
Rising	500	2023.6	
Falling	500	2023.8	23°C.
Falling	500	2023.3	25°C.
Rising	500	2024.0	
Rising	500	2023.7	
Falling	500	2023.5	26°C.
	Mean	2023.46	

Time of test 20 minutes, during which temperature of instrument increased 7° C.

The sample readings above, and 40 others taken at different heights of the scale, show that the readings of the instrument can be repeated with a precision of about 0.02 per cent. at the 500 mm. mark, and about 0.03 per cent. at the 100 mm. mark.

The observations prove that there is no effect analogous to pivot friction which would cause the readings to be different with a rising and a falling current. The temperature rise in twenty minutes with full load current is seen also to be small and to have no appreciable effect upon the readings.

From readings taken in the above manner with direct current the constant of the instrument was calculated from the formula $K = \frac{h}{I^2}$ where h is the height in inches at which the liquid column stands and I is the corresponding direct current in amperes. The value of K so obtained was 0.0000048223.

Assuming the square law to hold rigidly and using the above value of K, a direct reading scale was ruled on brass and fitted to the instrument. A week later the following sets of readings were taken on this scale, using direct current and a potentiometer and a 0.00001 ohm shunt as standards.

Reading on Meter in Amperes	Current Read with Potentiometer		Notes
1500	1501		Readings taken, instrument cold.
1300	1302		Readings taken, instrument cold.
1100	1100		Instrument slightly warm.
800	802		
600	601		
1800	1801	mean	The instrument was inclosed in an iron box to note if magnetic shielding produced any effect.
1800	1798	is	
1800	1801	1800	
1000	999		
200	196		
1700	1698		Current was dropping rapidly and last two readings are less reliable.
1700	1697		

We may conclude from the above that at the top of the scale the mean of a number of readings may be relied upon to be correct to better than 0.10 per cent.

Before the constant was obtained, and with another glass index tube in the meter than the one finally used, a set of relative measurements were made to determine if the meter read the same on direct current, and on alternating current of 25 cycles, 60 cycles, and 135 cycles per second. The meter was connected in series with a 1,000 ampere Kelvin balance. The currents were adjusted until the meter read at the 120 mm. mark on the

millimeter scale. The Kelvin balance was then read. The results obtained are given in the table below:

Observation at	Direct Current	Amperes Read by Kelvin Balance
120 mm. mark		985.0
120 mm. mark		985.2
120 mm. mark		985.1
	25 cycles per second.	
120 mm. mark		985.0
120 mm. mark		985.0
120 mm. mark		985.2
	60 cycles per second.	
120 mm. mark		984.6
120 mm. mark		984.6
	135 cycles per second.	
120 mm. mark		985.0
120 mm. mark		985.0

From this we may conclude that, within the limits of error of observation, the meter reads the same on direct currents and on alternating currents of commercial frequencies.

The temperature rise of the instrument above room temperature after running with various currents all above 1,000 amperes for at least six hours and between 1,500 and 2,000 amperes for at least one hour was found to be 16° C. This rise in temperature caused the zero to rise from one to two mm. The adjustment possible with the scale, however, permits the resetting of the zero. This resetting is generally not necessary except where great precision is required, and besides it does not entirely correct the small heat error because when the liquid stands high in the tube it is at room temperature and not at the temperature of the instrument.

The particular instrument on which the above tests were made had rather larger heat losses than given in the calculations above, partly because the axial length of the cells was greater than allowed in the calculation and partly because of heat losses in the copper and at the surfaces where the terminals were clamped on. It dissipated 56 watts with 2,000 amperes flowing.

Multiple Scale Meters.

It may be remarked here that the meter can be constructed so as to have several different scales instead of one. An inspection of Fig. 5 shows at a glance how this is accomplished. The figure is a diagrammatic top view of an ammeter of four sets of cells, (1), (2), (3), (4), each set having different diameter cells. There are four terminals, G, F, E, C. According as connection is made to different pairs of these terminals one or more sets of cells are brought into use, giving different current values at full scale reading. The following table shows the

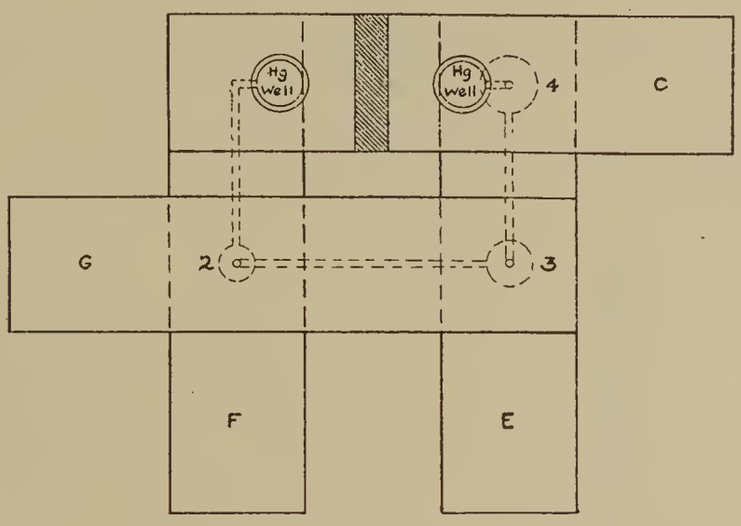


FIG. 5.

connections and the corresponding full scale current readings that might be obtained with each connection.

Connection	Cells in Use	Maximum Current
F — C	2-3-4	476
F — E	2-3	716
F — G	2	800
C — G	3-4	1250
E — G	3	1600
E — C	4	2000

The above series of maximum current values correspond to four cells which have the relative diameters 1, 2, 4, 5. Other series are readily worked out.

A meter was constructed and tested having three sets of cells as follows, Fig. 6.

The cells (1) and (2) had the relative diameters 4 and 5. The construction gave the following series of values:

Connection	Cells in Use	Maximum Current
A — B	1-2	688
A — C	1	880
B — C	2	1100

If we count the useful range of each scale from one-quarter to nearly full height of scale, the useful current ranges of the above series would be:

1st scale .....300-625 amperes
2nd scale .....400-800 "
3rd scale .....500-100. "

Other and perhaps better ranges might be obtained easily.

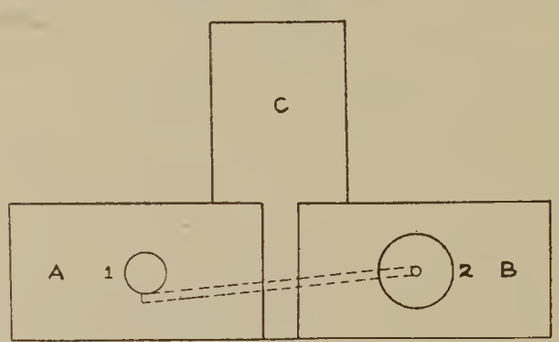


FIG. 6.

Proposed Application of Meter to the Absolute Measurement of Current.

The theory and tests described above give a guide to the design of a current meter to measure current in absolute measure. The measurement of electric current in absolute or c. g. s. units has been made by two methods; one in which a tangent galvanometer is used, and one in which some form of electrodynamometer or current weigher is employed. In the former, it is necessary to know the dimensions of the coil windings and the intensity of the magnetic field in which the suspended needle swings. In the latter, the dimensions of the fixed and movable coils must be known, also the value of the force used to oppose the electromagnetic forces. In both methods, the current measured is small and the value of currents as large as 1,000 amperes or more is known as a multiple of the small current which is actually

measured. In the method here proposed, a current as large as 1,400 c. g. s. units or 14,000 amperes would be measured, and the c. g. s. unit of current would be known then as a small fraction of this large current. By thus approaching the true value

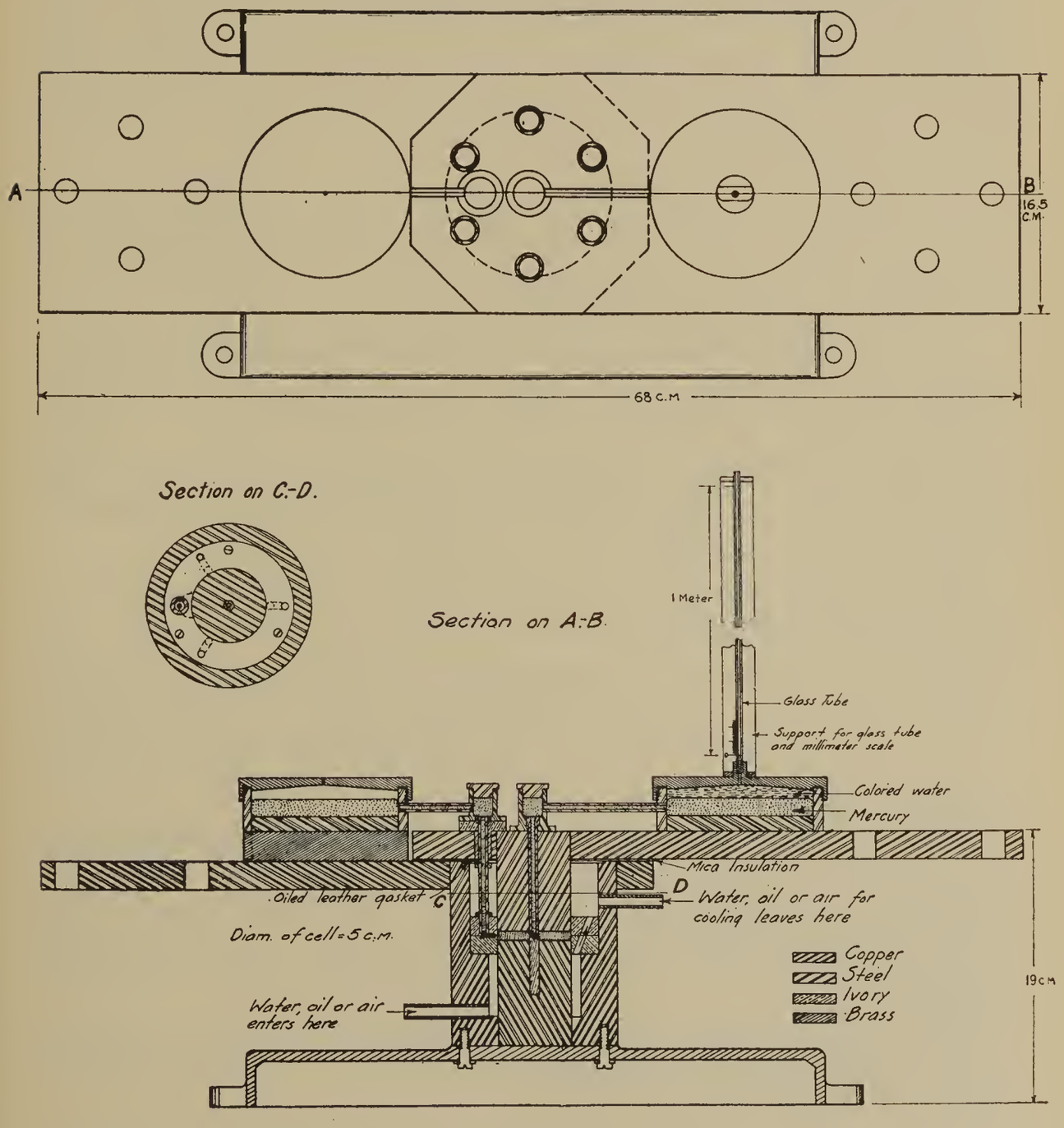


FIG. 7.

of the c. g. s. unit of current, from a high as well as from a low value of current, greater precision would be obtained, and the true value of the unit would become known with greater accuracy.

The design suggested for an absolute current meter is embodied in Fig. 7.

All the parts are designated in the drawing so that the figure is almost self-explanatory. The chief feature to note is that the current after having passed through the single cell returns in a tubular conductor which surrounds the cell. As there is no magnetic field in the interior space of a hollow conductor, the cell is entirely shielded from the influence of the field surrounding the return conductor.

The important assumption is made in the formula that the current density is uniform over the cross section of the cell. It is thought that this result can be satisfactorily attained by the construction shown in the figure.

It is further necessary that the current stream lines shall be straight and parallel to the axis of the electrodes and not be distorted where the mercury enters and leaves the cell. By the construction proposed in which the mercury enters and leaves by narrow slits of about 0.5 mm., this source of error would be unquestionably avoided.

The pressure produced would be determined by reading with a cathetometer the height to which the water column rises. By making the ratio of the cross section of the bore of the index tube to the area of the well extremely small, as indicated, the rise in the mercury itself could be made so small as to be neglected or at least easily allowed for as a very small correction.

The heat generated in the meter would be abstracted by a flow of oil in the space between the inner and outer conductors. Heating and expansions would be thus avoided, and very large current densities could be used, giving a large rise of the water column.

The formula for calculating the current in absolute measure would be (without corrections):

$$I = \left(\frac{\pi \, (R^2 - d^2)}{1 + \frac{2 \, d^2}{R^2 - d^2} \log_e \frac{d}{R}} \right)^{\frac{1}{2}} (h \, \delta \, g)^{\frac{1}{2}} \qquad (17)$$

where h is the height in cm. to which the water rises, δ the density of water at a particular temperature, and g the acceleration of gravity.

The first quantity in brackets is the constant of the instrument, to be obtained by an accurate determination of the two dimensions R and d; h might be easily 100 cms. and be measured to 0.01 cm., while δ and g are known with very great precision.

As an illustration of the use of eq. (17) assume for the quantities in the right hand member the following values, and calculate the current, I.

Choose,

R = 2.5 cms.

d = 0.25 cms.

π = 3.14159.

h = 100 cms.

δ = 0.998230 = density of water at 20° C.

g = 980.617 = acceleration of gravity in latitude 45°.

I = value of current in c. g. s. units.

Then

$$I^2 = \left[\frac{3.\ 14159[(2.5)^2 - (0.25)^2]}{1 + \frac{2 \times (0.25)^2}{(2.5)^2 - (0.25^2)} \log_e \frac{0.25}{2.5}}\right] \underline{\times\ 100 \times 0\ 99823 \times 980.617}$$

Call Δ the quantity in brackets.

Call γ the quantity underscored. Then

Δ = 20.387, γ = 978.87, and

$I = \sqrt{\Delta\gamma 100}$ = 1412.95 c. g. s. units of current or 14129.5 amperes.

This is a very large current, which could be gotten only from a large battery of storage cells. There would be connected, of course, in series with the current meter, a large shunt, and the drop over this shunt would be measured with a potentiometer when the meter measured the current. If the value of the standard cell is assumed known, then the resistance of the shunt is given, or if the resistance of the shunt is assumed known, then the value of the standard cell is given.

The watts that would be dissipated in the current meter for a rise of one meter of the water column would be about 100 for each millimeter of separation chosen between the two faces of the mercury cell.

It should be noted that the quantity d does not have to be very accurately measured, for if neglected altogether the error produced in the measurement of the current would be only about 1.84 per cent. Also, as the square roots of h, δ, and g enter the formula, the error made in measuring the current is only one-half the error made in measuring any one of these quantities. The error in the current measurement will be, however, almost directly proportional to the error made in measuring the radius R of the cell, hence the advantage in choosing the radius as large as possible with the current available for the measurement.

The temperatures of the different parts must be determined, of course, with considerable precision to correct for expansions of the faces of the cells and the change in density of the water column. These temperature measurements might be made accurately and easily with thermo-couples.

The above theory, design, and calculations of a large current meter have been given, not because it is hoped that investigators will use the method, good as it seems, for the absolute measurement of current, but because the principles laid down will apply equally well to the construction and use of a current meter of fine precision for measuring very large alternating currents. With proper attention to details of construction, a high accuracy could be obtained in determining the constant $\triangle$ of the instrument by calculations, thus avoiding the use of a costly equipment to obtain this constant experimentally with direct current, a shunt and a potentiometer.

It is hoped that those who are interested in determining the ratios of heavy current series transformers, and in making accurate measurements, for any purpose, of large direct or alter-taining currents, will avail themselves of this new method of current measurement which is at once relatively inexpensive, simple, and highly accurate.

Philadelphia, Pa.,
March 26, 1909.

Note.

Since the above paper was written, the writer received from Mr. John R. Carson, a graduate student in Princeton University,

a very complete and able mathematical analysis of the influence which would be produced upon the constant of the mercury ammeter by changes in the frequency of the current used. It is a well-known phenomenon that an alternating current does not distribute itself uniformly over the cross-section of a circular conductor, but crowds more or less toward the circumference. Mr. Carson investigated the influence that this so-called "skin effect" of an alternating current would have upon the pressure difference between the center and the circumference of a mercury cell of the ammeter. He expressed the conclusions of his analysis in a curve. The curve shows that the percentage change in the pressure difference is a function of both the frequency of the current and of the radius of the mercury cell. For a cell 2 cm. in diameter and a frequency of 500 cycles per second, the pressure difference is reduced below that which would be obtained with direct current only 0.028 per cent. Thus, this analysis, as well as the experiments made by the writer, confirm the conclusion previously stated that for all commercial frequencies the ammeter constant is very exactly the same for both direct and alternating currents.

A paper presented at the Fifteenth General Meeting of the American Electrochemical Society, at Niagara Falls, Canada, May 7, 1909; President E. G. Acheson in the Chair.

COOLING CURVES AND A NEW TYPE OF APPARATUS FOR THEIR AUTOGRAPHIC REGISTRATION.

By Edwin F. Northrup, Ph. D.

The present paper has for its objects:

To consider the advantages of autographic temperature recording apparatus when constructed upon proper principles;

To describe the principle, construction, and operation of a new type of autographic temperature recorder and its application to the registration of cooling curves, those of steel in particular;

To point out the relations between thermo-couples and resistance thermometers in giving sensibility and speed of registration in autographic recording;

To give some practical suggestions afforded by experiment, for autographically registering cooling curves of steel.

Autographic recording apparatus is so called to distinguish all those types of apparatus which record automatically the variations in any quantity other than by photographic means. Photographic recording apparatus has received a high development at the hands of many investigators and instrument manufacturers. When varying quantities are associated with manifestations of very minute amounts of energy, photographic registration of the variations would appear to be the only practical method. Thus, when a bolometer strip is slowly moved over the spectrum of the sun's light, the variations in the energy of different portions of the spectrum vary the deflections of a delicate galvanometer and these deflections have been photographically recorded with a beam of light reflected from the galvanometer mirror. No autographic recorder has yet been built for registering such minute variations in energy as this. But, as will appear later, autographic apparatus is now available which will automatically and accurately register energy variations where the available energy is exceed-

ingly small, and if the variations in the energy are not too rapid, autographic recording can be made to compete in nearly all cases with photographic recording in regard to sensibility and precision.

Confining our attention to autographic apparatus for registering variations in temperature, there are two distinct types to consider, one the deflection type, in which a deflection instrument of the milli-voltmeter type is used. For the greater portion of the time, the pointer of such an instrument is left free to deflect to a position of equilibrium and then, for a brief interval, is pressed down, causing a dot to be made upon a strip of paper moving slowly forward proportionally to the time. The depressions of the pointer are repeated at intervals, giving a line of dots. The briefness of the intervals between successive depressions is limited by the time it takes the system of the instrument to come to complete rest after it has been mechanically disturbed or electrically deflected. These intervals are from 10 to 12 seconds in instruments of the best type, when used with thermo-couples for measuring high temperatures. In the other, the balance type of autographic recorder, the marker rests at all times upon the advancing strip of record paper. In the recording of temperatures, whether thermo-couples or resistance thermometers be used, the forces available are not sufficient to move the pen over the surface of the paper against friction, and give any satisfactory degree of accuracy. When, therefore, temperature changes would tend to deflect the galvanometer, its small deflection or tendency to deflection serves to unlock forces which move the pen and at the same time restore the galvanometer to a balance at its open circuit zero position. An autographic recorder of this type can give records upon strips of paper of any desired width, and marked off in rectilinear coordinates.

Advantages of Autographic Over Photographic Recorders.

If the balance type of recorder is constructed simply and operates without any defects, and has great sensibility and accuracy, it will possess several decided advantages over photographic recorders. These advantages may be summarized as follows:

(a) If the instrument is once made accurate, its continued accuracy may be maintained, for the movements of the pen, as

will more fully appear later, are not dependent upon the permanence of the galvanometer constant. As the travel of the pen always rebalances the galvanometer to its open circuit zero, a small increase or decrease in its sensibility is ineffective. In all photographic recording, the galvanometer deflects. The constancy of the deflection with a given change in the variable being recorded, is dependent upon the galvanometer constant remaining unaffected through changes in its control or changes in the resistance of its own circuit.

The first or deflection type of autographic recorder does not, of course, share in the above advantage.

(b) The record is visible as it is being produced, and thus the autographic recorder is at the same time an indicator of the temperature from moment to moment. Thus processes can be controlled which require to be regulated in accordance with the momentary temperatures indicated.

(c) The marking pen can be made to draw a very fine line instead of the rather broad band which a spot of light usually traces, and hence full benefit may be obtained from the inherent precision of the recorder.

(d) The movements of the pen can be made to take place in a right line in strict proportion to the variations of the quantity to be recorded. Thus, if a resistance thermometer is used to measure the temperature changes as they occur, the pen of an autographic recorder can easily be made to move proportionally to the temperature changes even though the resistance of the thermometer does not change proportionally to the temperature variations. In photographic recording this would be difficult if not impossible where the temperature changes measured are large. The first type of recorder does not share in this advantage.

(e) The record when drawn is complete, and may be made continuous on a strip of paper of unlimited length. In photographic recorders the record must be developed. This last merit of autographic recorders is of immense importance where they are to be used in connection with industrial processes.

(f) Lastly, in the new type of recorder to be described, the carriage carrying the pen, without affecting the precision or sensibility of the recording, can be made to move in response to

temperature changes with a force of one or more pounds. With such a force at one's disposal, electrical contacts can be made with certainty which may be used to move heavy apparatus to perform various functions, such as shutting off or on gas used to heat the place where the temperature is being taken. Thus, the autographic temperature recorder with little change in construction can be made equally well to control temperatures and maintain them constant.

A New Type of Autographic Recorder.

The advantages of autographic over photographic recorders, when these are used for recording temperature changes or temperature differences, are mostly offset if the apparatus is not at the same time susceptible of high precision and great sensibility. These last cannot be secured in the balance type of autographic recorders, if to unlock the forces which move the recording pen the galvanometer pointer has to play the part of a delicate relay and do any work whatever in making a contact. If its pointer, when the galvanometer starts to deflect, touches any kind of a contact, stationary or moving, and the forces which move the pen are released by the action of an electric current which flows between the galvanometer pointer and what it touches, then the release of these forces will be dependent upon the certainty and the regularity of the contact so made.

If great sensibility is needed, the galvanometer pointer can only press the contacting surfaces together with an exceedingly feeble force. The magnitude of this force will depend upon the degree of unbalance of the galvanometer, while the determining factor as to whether or not contact is made, is dependent only partly upon the force of contact and largely upon accidental circumstances, such as the cleanness of the contacting surfaces, and accidental vibrations which may contribute to strengthen or to weaken the force of the contact. Regularity and precision in the results can only be secured by so arranging matters that the pointer of the galvanometer can move from one position to another with absolute freedom, being restrained by the torsional force of its suspension only. In the type of balance recorder here described, the galvanometer is left absolutely free to deflect

a short distance to the right or to the left, and, without itself doing any work in making a contact, determine the strong movement of the recording pen. The pointer of the recorder acts, not as a contacting device, but as a *selector* which determines, *when contact is made by means independent of the galvanometer,* whether energy shall flow in a circuit E or another circuit F. If energy flows in the circuit E, the pen moves a small but definite space interval to the left, and if energy flows in circuit F, the pen moves the same definite space-interval to the right. If the pointer does not deflect at all, no contact can be made by the independent contacting device, energy will not flow in either circuit E or F, and hence the pen will not move. The pen, therefore, when it moves, moves one step at a time, and when the galvanometer is permanently unbalanced in one direction the pen takes a step each time that the contacting device makes a contact.

The method of moving the pen is, therefore, a step by step method, and if the paper is advancing under the pen with the time, the line drawn by the pen is a terraced line. The steps of the terraced line are equal in width to the length of each step of the pen, which in the present type of recorder is 1/48 of an inch. If contact occurs once in a second, the pen will therefore have a maximum speed of travel of ten inches in eight minutes, or in sixteen minutes if contact occurs every two seconds. This latter speed has been found sufficient for most cases of temperature recording. For special cases, where temperature changes rapidly, a greater number of contacts or longer steps or both can be obtained and the travel of the pen be made to keep up with very rapid changes of temperature if such occur. The shortness of the steps, being 1/480 of the width of the record sheet, makes the record line practically a smooth one, and a theoretical accuracy of recording of one part in 480. The contacting device can be used with a galvanometer of very high sensibility. The manner in which the periodically contacting device operates will be made clear by a reference to Fig. 1.

The dot, p, represents the platinum tip of the galvanometer pointer, which in practice is about 2½ inches long. The piece marked c is a piece of silver which is moved upwards at intervals of two seconds or less and clamps the end of the pointer, p,

forcibly for one-fifth of a second between itself and the upper piece. This consists of two silver parts, a and b, and an ivory piece 1/16 of an inch in width marked i. If, when c moves upward, the pointer is under a, energy from Ba flows in the E circuit, and if under b, energy flows in the F circuit, while if it is under i, no energy flows from Ba.

If the galvanometer continues to remain balanced, so that its pointer is always under i, the pen will draw a perfectly straight line upon the record sheet as it moves forward with the time, this movement being governed by a clock and at any desired speed.

Now it is evident that as the piece c releases the galvanometer pointer, after having pressed it against its upper contact, it may

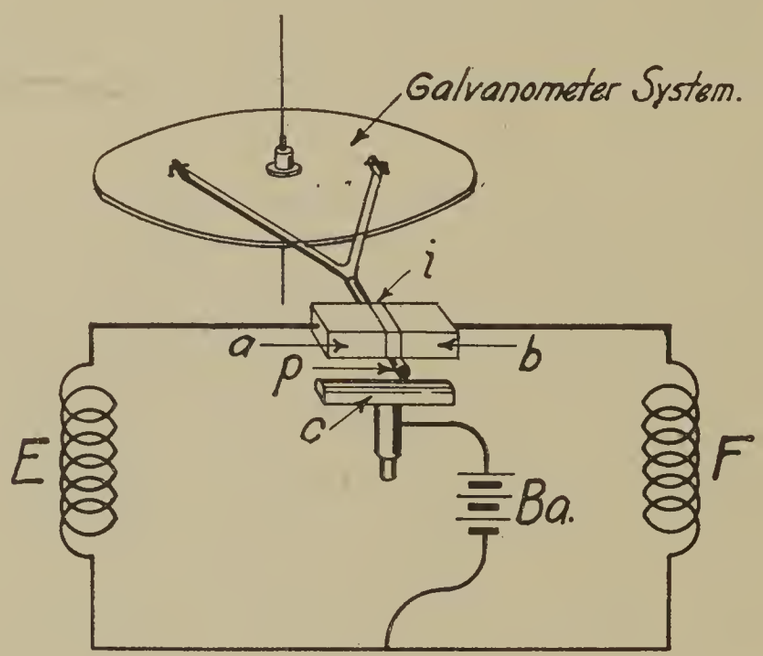


FIG. 1.

give the pointer a slight disturbance either to the right or to the left. If, however, the galvanometer is damped to be just aperiodic, it will return, after its pointer is released, to its position of equilibrium in a time which depends only upon its natural period of swing in one direction. The contacting piece, c, must leave the pointer free between successive contacts for a period at least as great as the natural period of swing of the aperiodically damped galvanometer. Thus, for speed of action the galvanometer system should have the smallest practical moment of inertia so that for a given sensibility its damped period of swing may be as short as possible.

For most all requirements of temperature recording, the sensibility and quickness of the galvanometer may be made ample without special attention to this requirement and other considerations, of which robustness is a chief, have led to the design of a flat coil galvanometer of large moment of inertia. The period of the standard type is one and one-fifth seconds, and contacts are made at intervals of two seconds and continue one-fifth of a second.

The contact piece, c, is moved by a small plunger magnet operated by a contact on the clock which is used to drive the paper. The energy paths E and F include each an iron-clad electromagnet, one serving to turn a rod, upon which is cut a screw thread, in one direction, the other in the opposite direction. When this rod turns, a nut is screwed towards the right or left, according to the direction of turning of the rod. This nut carries both the pen and a sliding contact. This latter moves over a slide resistance of special construction and restores the galvanometer to a balance at the same time that the pen—an ordinary stylographic pen—traces a line.

The galvanometer used is a differential galvanometer. The method by which it is deflected as the temperature changes, and the principle on which the balance is restored, can be described best by considering the diagrammatic view of the electrical connections (Fig. 2). While the recorder is equally applicable to recording temperatures indicated by thermo-couples or resistance thermometers, the latter have been found the more generally useful, and the diagram, Fig. 2, shows the circuits when the recorder is to be used with a resistance thermometer. There are two sets of circuits for the apparatus, the set, V, which has to do only with the measurement, and the set, W, which has to do only with moving the pen and the contact which restores the balance.

In the measuring circuits, V, the resistance from a to b is the slide resistance, which we will call, l. The two windings of the differential D'Arsonval galvanometer are marked g_1 and g_2. The resistance X is a platinum or other wire of high temperature coefficient, which constitutes the thermometer, and varies in resistance with the temperature. R is a resistance of manganin, of negligible temperature coefficient. The contact, p^1, can be

moved by hand, or automatically in the recorder, over the slide resistance l. Ba is a source of current, usually two dry cells. A, B and C are lead wires connected to the thermometer, and joining the binding posts a_1, c_1, b_1 to a_{11}, c_{11}, b_{11}, as indicated.

A differential galvanometer is balanced when the resistance, which includes one-half of its differentially wound coil, between the battery contacts, is equal to the resistance which includes the other half of its coil between the battery contacts, or when

$$c + g_1 + R + B = l - c + g_2 + A + X. \qquad (1)$$

If by construction we make $g_1 = g_2$, and $B = A$, then we have,

$$2c + R - l = X \qquad (2)$$

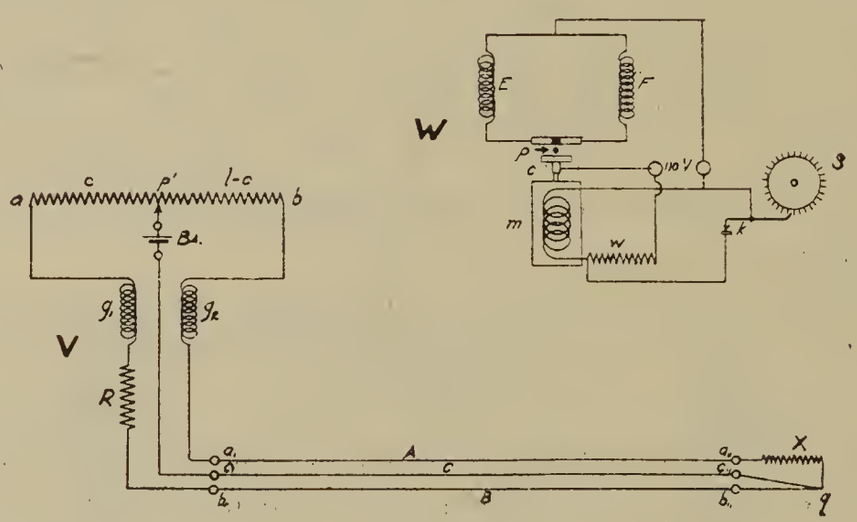


FIG. 2.

Since $R - l = K$, a constant, we have

$$c = \frac{X}{2} - \frac{K}{2}$$

or

$$\delta c = \frac{\delta X}{2} \qquad (3)$$

Thus, to maintain the galvanometer balanced, when X varies, we must slide the contact p^1 along the resistance l. The resistance, c, will then vary proportionally to the resistance X and half as fast.

It will be observed that, if the leads, A and B, are made of equal resistance, the galvanometer is balanced independently of

the resistances of the three leads A, C, and B. The thermometer may be, therefore, at any distance from the recorder without affecting the accuracy, and be joined to it with only three lead wires.

As is well known, platinum wire does not change its resistance in exact proportion to change of temperature. To make the recorder pen move proportionally to temperature changes and not to resistance changes, it is only necessary to grade, by experiment, the resistance of the slide resistance l. This resistance, which may be 10 ohms or more, is made by winding a small silk insulated manganin wire upon a drill rod about one-sixteenth of an inch in diameter. The wire forms a spiral of 60 or more turns to the inch. The drill rod is pulled out and the spiral winding is cemented in a groove in a strip of hard rubber. The insulation is buffed off the surface of the spiral where the contact, p^1, bears upon it. In this manner, a wire of substantial size may be employed, and, in the 10-inch length, which is used, have some 20 to 30 times the resistance of the same size of wire stretched out straight. The grading of the resistance is made easily by winding the spiral upon a slightly tapered drill rod, and fine adjustments are effected by rubbing with emery cloth.

The circuits, W (Fig. 2), serve in the operation of the contacting piece, c, and in the recorder-mechanism proper. The contact, k, is opened at intervals of two seconds by the clock wheel, S. This takes the shunt off the magnet, m, for one-fifth second, allowing the magnet m to raise c and press the pointer, p, in contact with the upper piece. The magnets E and F by a special mechanism move the pen to the right or left, and at the same time slide the contact p^1 over the slide resistance, l, until a balance of the galvanometer is restored.

Returning to the circuits V we wish to inquire what should be the resistance of each of the two windings, g, of the galvanometer coil to give a maximum sensibility. Analysis shows that, if X is the resistance of the thermometer, and the number of watts which it is allowable to expend in the thermometer is a fixed quantity, that one should make the resistance of the thermometer equal to the resistance of one side of the differential galvanometer coil; namely, we should have $X = g$.

Further, as it is often desirable to be able to shunt the slide

resistance, l, to change the range of the recorder scale, we wish to inquire if c changes proportionally to X when p^1 is moved so as to maintain a balance of the galvanometer. This we can prove to be the case by the following considerations, which are given here, as they apply generally to cases where a differential galvanometer is used to measure a resistance by moving a contact over a slide resistance for obtaining a balance.

The signification of all the symbols used will be fully understood by reference to Fig. 3 without further explanation.

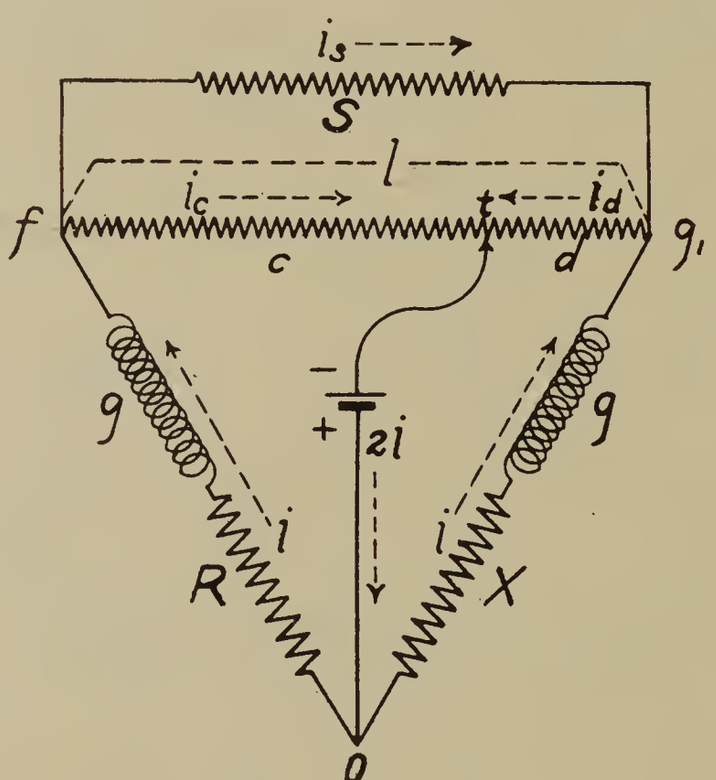


FIG. 3.

By Kirchoff's laws

$i - i_c - i_s = 0$ are the currents which enter and leave f. (1)

$i + i_s - i_d = 0$ are the currents which enter and leave g_1. (2)

$iX + i_d d = E$ is the e. m. f. in circuit $0 - g_1 - t - 0$ (3)

$iR + i_c c = E$ is the e. m. f. in circuit $0 - f - t - 0$ (4)

$i_s S + i_d d - i_c c = 0$ is the e. m. f. in circuit $f - g_1 - f$ (5)

Subtracting (4) from (3) gives

$$i (X - R) + i^d d - i_c c = 0 \quad (6)$$

From (1) $i_c = i - i_s$ (7)

From (2) $i_d = i + i_s$ (8)

Putting the values of i_c and i_d in (6) gives

$$i\,(X - R) + di + di_s - ci + ci_s = o \text{ or} \qquad (9)$$

$$i_s\,(c + d) + i\,(X - R) - i\,(c - d) = o \qquad (10)$$

Putting the values of i_c and i_d in (5) gives

$$i_s S + di + di_s - ci + ci_s = o \text{ or}$$

$$i_s = \frac{i\,(c - d)}{S + c + d} \qquad (11)$$

Also from (10) we have,

$$i_s = \frac{i\,(c - d) - i\,(X - R)}{c + d} \qquad (12)$$

Equating the second members of (11) and (12) we derive

$$X = \frac{R\,(c + d + S) + S\,(c - d)}{S + c + d}. \qquad (13)$$

In (13) replace d, by its value l — c and we obtain

$$X = \frac{2\,c\,S}{S + l} + \frac{R\,(l + S) - lS}{S + l} \qquad (14)$$

The last term of (14) is a constant.

Call this K and we have finally

$$X = \frac{2\,c\,S}{S + l} + K \qquad (15)$$

Differentiating (15), we find,

$$\frac{\delta X}{\delta c} = \frac{2\,S}{S + l} \text{ or } \delta c = \frac{S + l}{2\,S}\,\delta X \qquad (16)$$

Equation (16) shows that c varies proportionally to X and only $\frac{S + l}{2S}$ as fast.

This result means that in the case of a uniform slide resistance, this resistance may be given any convenient value greater than the minimum allowed. It may be shunted then to give the particular temperature range desired with a length of resistance of ten inches.

When the resistance, l, has been tapered considerably to correct for a non-linear coefficient, the shunt, S, must be a high resistance and can only be used to modify the temperature range by small amounts. This result, which is not rigidly true for a

shunt on the slide wire of a Wheatstone bridge, is of considerable value in resistance thermometry.

The mechanical features and arrangement of parts of the recorder will not be described, as they are, for the most part, clearly shown in the accompanying illustration of the complete apparatus (Fig. 4).

It will be noted that the paper moves forward over an apron, and is driven by the clock on the left. The paper is a continuous

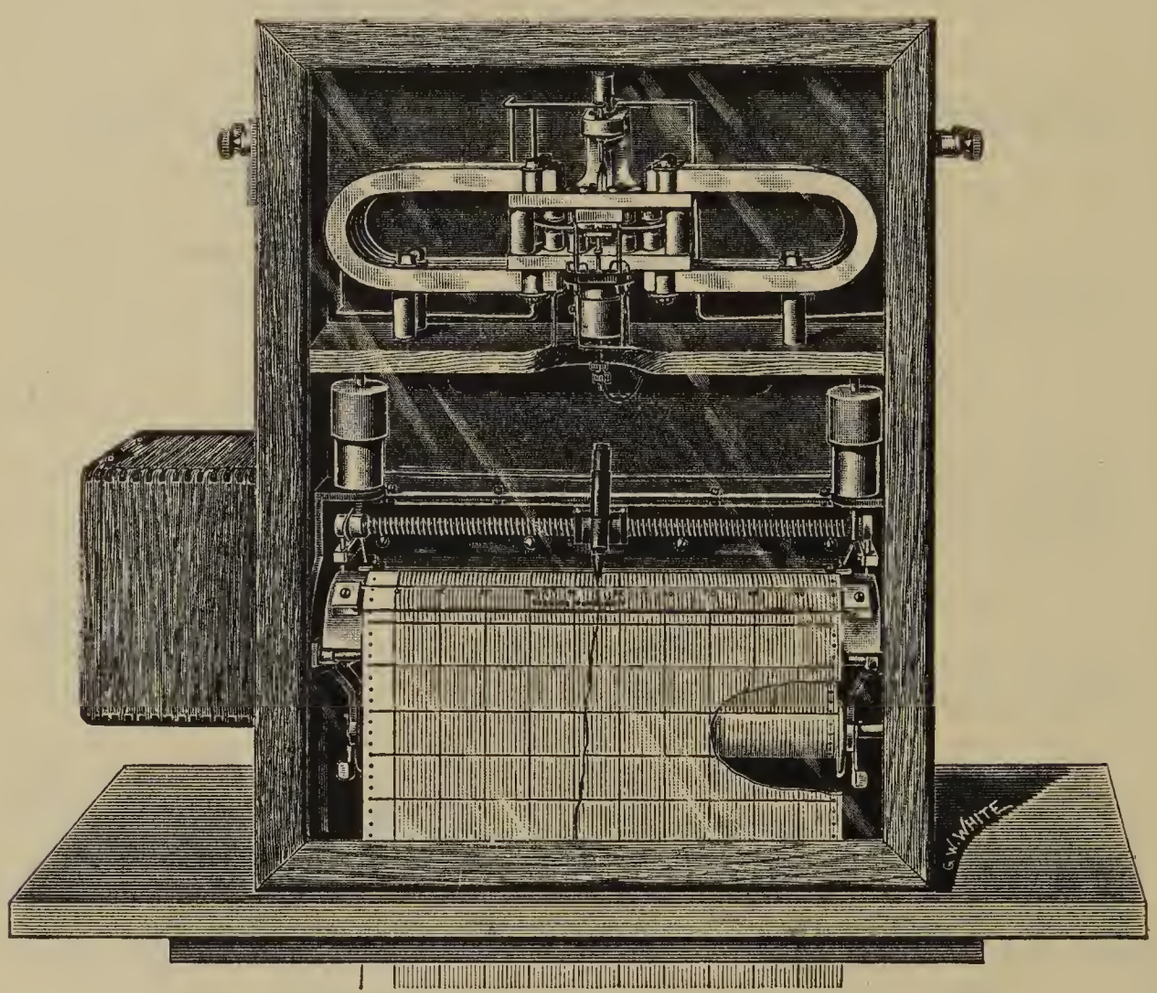


FIG. 4.

band of cross section paper, having a hundred divisions in the direction of its width. The normal sped of travel of the paper is three inches per hour, but this speed can be arranged to be greater or less if desired.

The complete recorder consists of four essential parts: a differential galvanometer, with a plunger magnet attached to it, for operating periodically the contactor; an eight-day clock, which drives the paper and operates the contacting plunger-magnet; a

simple mechanism consisting of a screw and two electromagnets of the plunger type for traveling the pen and the balancing contact; and a paper drive, moved by the clock, which feeds a continuous band of paper off a roll and over an apron carrying it under an ordinary stylographic pen. All parts of the recorder are made up as separate, interchangeable units, which may be easily assembled, disassembled, or replaced. The uninterrupted operation of the apparatus, so essential in industrial uses, is assured by the manner in which it is constructed, and the ease with which replicas may be effected of any parts which fail.

Cooling Curves.

Newton's so-called law of cooling is, that a body placed in still air at a temperature lower than itself, cools at a rate which is proportional to the temperature difference between itself and the surrounding medium. If bodies cooled in this way uniformly or even approximately so, the curves representing their cooling, with temperature as ordinates, and time as abscissae, would be smooth curves convex towards the axis of X which they would approach asymptotically. But, cooled over a considerable range of temperature, few bodies show such smoothness in their curves. Many solids and liquids exhibit at certain points jogs and inflections in their cooling curves. These variations from smoothness in the cooling curve of a body, when accurately plotted, can be made to yield important information regarding the energy transformations which take place as the body cools. Inflections in the cooling curve are at once an indication and a partial measure of such energy transformations. "Just as the heat evolved in the freezing of water arrests the fall of temperature, so every change, chemical or physical, which occurs within any cooling mass (be it an aqueous solution, an alloy, or a rock-mass) as it passes any particular temperature or range of temperature, will in general cause either an evolution or an absorption of heat, in short, will be accompanied by some thermal action, and this will affect the progress of the cooling, and thus will record itself automatically on the cooling curve." (H. M. Howe, "Iron, Steel and Other Alloys," page 19.)

An autographic temperature recording apparatus, which is at

once sensitive, accurate and capable of precisely duplicating its results, can afford therefore the chemist and the metallurgist a simple, rapid, and delicate means of investigating the energy transformations in bodies. But to obtain from a recorder its best performance, and to know that the inflections recorded upon the curves occur at the precise moment and temperature that the energy transformations, under study, really occur, necessitates a careful observance of certain experimental conditions. The more essential of these conditions, which are frequently lost sight of, deserve our attention.

Though the most direct and frequently employed method is to plot the temperature, θ, against the time, t, there are several other methods by which cooling curves may be represented, some of which can be drawn autographically. These various possible methods of obtaining cooling curves have been described very fully by G. K. Burgess, in the November, 1908, number of the Bulletin of the Bureau of Standards.

It is shown there that the following forms of curves may be plotted:

I. θ vs t .....Temperature Time Curve.

II. θ vs $(\theta - \theta')$.....Differential Curve.

III. θ vs $\frac{d\theta}{dt}$ .....Temperature-Rate Curve.

IV. θ vs $\frac{dt}{d\theta}$ .....Inverse Rate Curve.

The first is the ordinary and most used type of curve. The second is obtained by cooling under the same circumstances, as the sample body under observation, another neutral body such as a mass of platinum, which cools in a regular manner without any energy transformations. Two thermometers register the difference in temperature between the sample and the neutral body, while a third thermometer registers the temperature of the sample.

The third form of cooling curve may be derived by a graphical construction from the first, by finding the rate of cooling over an interval dt obtained by finding the value $\frac{d\theta}{dt}$

The fourth type of curve, which was used by Osmond, in France, to show the recalescence points in iron and steel, is obtained when the rate at which a mass cools through a given number of degrees is plotted against its temperature. This form of curve may be regarded as the reciprocal of the temperature-rate curve.

Of these four forms of curves, a single autographic recorder is only capable of giving the first. By employing two autographic recorder-mechanisms, the paper may be caused to move proportionally to the temperature of the sample, and the pen be made to move proportionally to the difference in temperature between the sample and a neutral body, and thus θvs$(\theta - \theta')$ may be recorded autographically. However, while this last result is possible, it is complicated and unnecessary, although by its means very small changes in the cooling of the sample may be revealed.

With a highly sensitive and accurate recorder, the temperature range of which can be modified at will, the first form of curve, in which temperature is plotted against time, will yield all the information desired, and in a manner most simple and direct. We shall limit therefore our discussion and examples shown entirely to this form of cooling curve.

Use of Resistance Thermometers Versus Thermo-couples in the Autographic Recording of Cooling Curves.

In the types of autographic recorders thus far devised, there is for each type of recorder, when used with a particular kind of thermometer, a certain maximum rate at which the sample mass may be cooled through the temperature range to be studied. The maximum rate of cooling possible will depend ultimately upon the torque given to the galvanometer by the variation in the temperature with the particular type of thermometer used. The reason for this is as follows: In the type of autographic recorders like the one above described, and the temperature recorder of the Siemens and Halske type, a portion of the record is made upon the record sheet at regularly recurring intervals. The manner in which this is accomplished has been fully explained for the step by step type of recorder described above.

In the Siemens and Halske recorder, which consists of a sensitive needle galvanometer used with a thermo-couple, the freely swinging needle is depressed, as stated above, by a metal piece at regularly recurring intervals so that the point of the needle makes a succession of dots upon the record sheet, the locus of which constitutes the recorded curve. In both of these types of recorders, and others operating on similar principles, the galvanometer system must be made aperiodic to give the maximum speed of working. Now, the time which must elapse between each successive contact or depression of the needle cannot be less than the natural "dead beat" period of the galvanometer system. If this natural period is, for example, ten seconds, then the needle may be depressed every ten or twelve seconds. This means that any increasing or decreasing deflections due to temperature variations, which may occur in the twelve-second interval when the needle is not being depressed, are not recorded. Thus, the shorter the natural period of the galvanometer, the more frequently can be made the successive portions of the record, and, in taking cooling curves, the more rapidly the sample may be cooled.

Thus, the possible maximum rate at which a sample may be cooled is directly proportional to the number of contacts which can be made per second. If V is the velocity of cooling, n the number of contacts per second, T the natural "dead beat" period of the galvanometer, and s the torsional force of the control, we have: $n = \frac{1}{T}$, and as $V \propto n$, and $T \propto \sqrt{\frac{I}{s}}$ very approximately, we have $V \propto \sqrt{s}$. But the torsional force which may be given to the controlling spring or suspension may be increased, without changing the galvanometer deflection, in direct proportion to the torque, q, produced upon the galvanometer system when a certain temperature acts upon the thermometer or thermo-couple. Hence we have the relations

$$V \propto n = \frac{I}{T} \propto \sqrt{s} \propto \sqrt{q}.$$

Or, in words, the velocity with which a sample may be cooled, and its curve be recorded autographically, is directly proportional

to the square root of the force acting to deflect the galvanometer which is produced by any type of electric thermometer when submitted to a particular temperature.

It is necessary now to consider the relative torque exerted by a resistance thermometer and by a thermo-couple to deflect a galvanometer. We will then be in better position to decide regarding the comparative usefulness of resistance thermometers and thermo-couples for autographically recording cooling curves.

Let Fig. 5 represent the connections of a differential galvanometer arranged to measure, by the extent of its deflection, the changes in a resistance X.

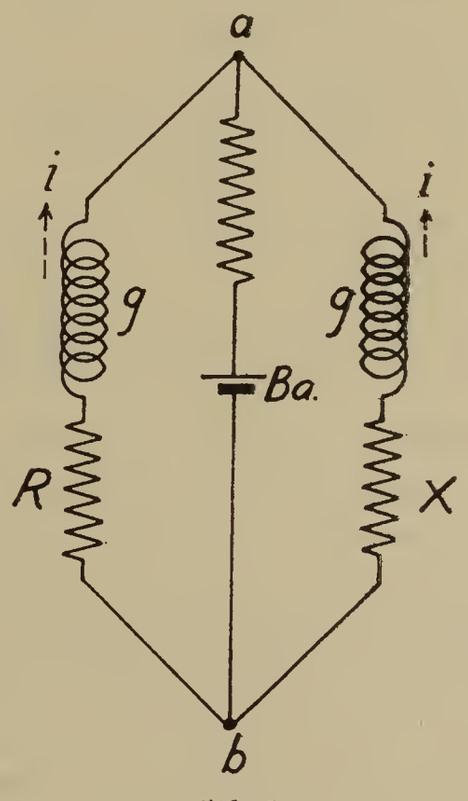


FIG. 5.

Let X be the resistance of a resistance thermometer at any temperature θ.

Let R be a fixed manganin resistance, and let g, g, be the two equal differential windings of the galvanometer coil. The galvanometer will be balanced and the deflection zero when $R + g = X + g$.

If X_0 is the resistance of the thermometer at 0° C., then $X_1 = X_0(1 + k\theta_1)$ is its resistance at θ_1 degrees. Let $R = X_2 = X_0(1 + k\theta_2)$ be the value of R for which the galvanometer is balanced.

The torque on the galvanometer system is

$$q = K(i_1 - i_2) \qquad (1)$$

where K is a constant and i_1 and i_2 are the currents in the right and left hand windings of the coil, respectively.

Let E be a constant potential difference maintained by the battery Ba, between the points a and b (Fig. 5).

Then $i_1 = \frac{E}{X_1 + g}$, $i_2 = \frac{E}{R + g}$, whence we derive,

$$q = \frac{K\ E\ (R - X_1)}{(X_1 + g)\ (R + g)} \qquad (2)$$

Or as, $E = i_1(X_1 + g)$ we have,

$$q = \frac{K\ i_1\ (R - X_1)}{R + g} \qquad (3)$$

In (3) give R its value $X_2 = X_0(1 + k\theta_2)$ and X_1 its value, $X_0(1 + k\theta_1)$ and we have,

$$q = \frac{K\ i_1\ X_0\ k\ (\theta_2 - \theta_1)}{X_2 + g} \qquad (4)$$

If we wish to compare the torque, as expressed by equation (4), given by a resistance thermometer, with the torque given by a thermo-couple acting under conditions which are comparable with the first, we must use the same galvanometer with the thermo-couple as with the resistance thermometer.

To do this, connect the two windings of the differential galvanometer in series with each other and the thermo-couple. Also add in series with the galvanometer an external resistance, r, of manganin.

This last is often necessary because the percentage change in the resistance of the total circuit must remain small if the temperature is to be measured accurately by the deflection of the galvanometer. Without r in the circuit, the percentage variation in the resistance of the circuit will be considerable, due to changes in the resistance of the thermo-couple-leads with different depths of immersion, and to changes in the resistance of the galvanometer coils with changes in room temperature.

Let Fig. 6 represent these connections. The e. m. f., e, developed by the thermo-couple is proportional to the difference

in temperature between the hot and cold junctions, or $e = A(\theta_1 - \theta^1)$, where A is a constant which depends upon the kinds of metals which are opposed to each other. A is the volts which is developed by a difference in temperature of 1° C. between the hot and cold junctions.

When the temperature of the hot junction is θ_1, the current in the galvanometer circuit is,

$$C_1 = \frac{A\ (\theta_1 - \theta^1)}{2g + r} \tag{5}$$

and when the temperature of the hot junction is θ_2,

$$C_2 = \frac{A\ (\theta_2 - \theta^1)}{2g + r} \tag{6}$$

Then the increase in the torque when the temperature changes from θ_2 to θ_1 is,

$$q_1 = 2K(C_2 - C_1). \tag{7}$$

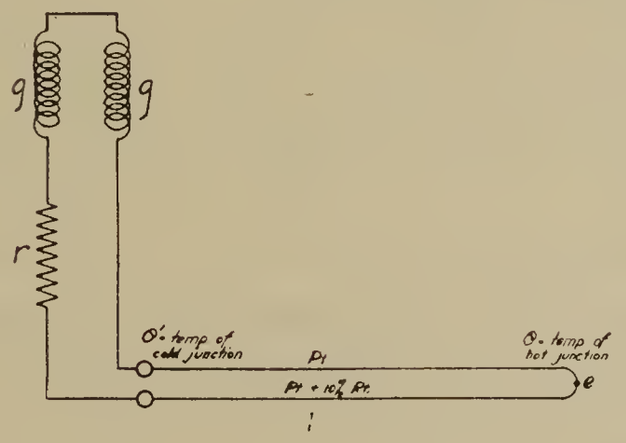


FIG. 6.

Here 2K is now the constant of the galvanometer because both windings contribute to the deflection.

From equations (5) (6) and (7) we have

$$q_1 = \frac{2K\ A\ (\theta_2 - \theta_1)}{2g + r} \tag{8}$$

Comparing equations (4) and (8) we derive

$$\frac{q}{q_1} = \frac{i_1\ X_0\ k\ (2g + r)}{2\ A\ (X_2 + g)} \tag{9}$$

Equation (9) gives the ratio of the torques acting upon the *same* galvanometer, first, when used as a differential instrument

with a resistance thermometer, and second, when used as an ordinary galvanometer with external resistance and a thermo-couple.

We shall give two numerical examples, one in which the conditions are made favorable for the thermo-couple, and one in which the conditions are arranged for both the resistance thermometer and the thermo-couple, as the best practice allows when cooling curves of steel are to be autographically drawn.

For the first case take

$A = 11 \times 10^{-6}$, the e. m. f. of Pt vs Pt + 10% Rh, for 1° C, difference in temperature between hot and cold junctions.

$X_0 = 1$ ohm at 0° C.

$k = 0.0036$, the coefficient of pure platinum.

$g = 35$ ohms.

$r = 0$.

$i_1 = 0.05$ ampere, a current which will not appreciably heat the resistance thermometer.

$X_2 = X_0(1 + 0.0036 \times 1000) = 4.6$ ohms, = the resistance of the thermometer at 1000° C,

$$\text{Then } \frac{q}{q_1} = \frac{.05 \times 1 \times .0036\ (2 \times 35 + 0)}{2 \times 11 \times 10^{-6}\ (4.6 + 35)} = 14.5 +$$

Thus, when the galvanometer has no external resistance, and only 1 ohm, at 0° C., of resistance wire is used, there will be nearly 15 times as much torque with a resistance thermometer as with a Pt vs Pt + 10% Rh thermo-couple.

For the second case, take,

$A = 11 \times 10^{-6}$.

$X_0 = 5.5$.

$X_2 = 5.5 \times 4.6 = 25.3$.

$k = 0.0036$.

$g = 35$. $2g = 76$ ohms, is the resistance of Siemens and Halske's thermo-couple galvanometer.

$r = 270$ = external resistance used by Siemens and Halske in their thermo-couple galvanometer.

$i_1 = 0.2$. This current may be used if the thermometer is calibrated with the same current it is used with.

$$\text{Then } \frac{q}{q_1} = \frac{.2 \times 5.5 \times .0036\ (2 \times 35 + 270)}{2 \times 11 \times 10^{-6}\ (25.3 + 35)} = 1015.$$

Thus, a resistance thermometer, as used in practice, when compared with a thermo-couple, as used in the best practice, gives over 1,000 times the torque that the thermo-couple gives. This means that for equal sensibility, to detect temperature changes, the galvanometer, used with the resistance thermometer, could have $\sqrt{\frac{1}{1000}}$ or 0.03 times the period of the same galvanometer used with a platinum-platinum rhodium thermo-couple, and an external resistance sufficient to maintain the percentage variation in the resistance of the circuit within the limits of good practice. A galvanometer of 0.3 second period, used with a resistance thermometer, would be as sensitive to temperature changes as it would be with a period of ten seconds if used with a thermo-couple.

The value for the constant, A, is given for other combinations of metals, often used for thermo-couples, in the table below:

Platinum vs. Platinum + 10% Rhodium ...	$= 11 \times 10^{-6}$
Nickel vs. Constantan	$= 23 \times 10^{-6}$
Iron vs. Copper	$= 53 \times 10^{-6}$
Constantan vs. Copper	$= 58 \times 10^{-6}$
Nickel vs. Copper	$= 61 \times 10^{-6}$
Iron vs. Constantan	$= 67 \times 10^{-6}$
Iron vs. Nickel	$= 75 \times 10^{-6}$

It should be noted that the torque which a given thermo-couple will produce in a particular galvanometer, with a given temperature difference between the hot and cold junctions, is a fixed and invariable quantity, while with a resistance thermometer the torque will increase with the current passed through the thermometer. For special conditions this current may be made large without affecting the precision, by calibrating the thermometer with the same current with which it is afterward to be used. In the case where R, Fig. 5, or Fig. 3, also is made a resistance which changes with the temperature, and the differential galvanometer is used in this manner with two thermometers to measure not an absolute temperature but a *difference* in two temperatures, the current used will heat the two thermometers alike, and consequently can be very large, giving great sensibility. This conclusion was amply justified by the construction of an autographic recorder similar to the one described

above, which recorded the temperature difference between the ingoing and the outgoing water of a human calorimeter where the maximum temperature difference was only 4° C., and the accuracy required was ½ per cent. The recorder was sensitive in this case to 0.018° C., and the period between contacts was two seconds. The record was drawn in rectilinear coordinates, on a sheet where eight inches corresponded to 4° C. This performance, using thermo-couples, would be impossible.

The claim is often made for the thermo-couple that its mass is very small and consequently will measure changing temperatures without appreciable lag. But in taking cooling curves the thermo-couple has no advantage over the resistance thermometer in this respect:

If the sample is extremely small, it will cool more rapidly than any autographic recorder can follow the cooling, and autographic recording cannot be made with either thermo-couples or resistance thermometers, and if the sample is of moderate diameter,

FIG. 7.

say one-half inch or more, and can be made two or more inches in length, then the resistance thermometer may be made long and of small diameter, and so be as free from lag as the thermo-couple.

Fig. 7. is a view of a resistance thermometer constructed for taking cooling curves of steel to show the recalescent points. Its resistance is 16.9 ohms at 620° C. The length of the working resistance is three inches and the diameter of the stem, to be inserted in a hole bored parallel to the axis of a cylindrical sample, is but ⅛ inch. The platinum wire is protected by a very thin walled porcelain tube. This thermometer plunged from room temperature into an oven at 500° C. would assume the temperature of the oven completely in less than two minutes. A thermo-couple properly protected would be little, if any quicker acting, and would give to the galvanometer, without any external resistance, only about $\frac{1}{200}$ the torque. With longer samples, a larger resistance

thermometer constructed in the same way could be made and it will be apparent from what has been shown above, that if l is the length of the thermometer, the possible speed of cooling can be increased proportionally to the $\sqrt{l}$. This increase of speed is a great advantage where many samples are to be tested.

It should be noted, also that with the resistance thermometer, there is no cold junction to consider while with the thermo-couple, the accuracy with which the various points on the curve are located in actual degrees is no better than the accuracy with which the cold junction is held at a constant and known temperature. In examining several samples of steel for their recalescent points, it is evident that one must know that variations in the positions of the recalescent points of the different samples is due to the different qualities of the samples, and not to variations, during the progress of the tests, of the temperature of the cold junction.

A most important advantage of the resistance thermometer, when used with the autographic recorder, for taking cooling curves, is the ease with which any portion of a cooling curve, extending over a considerable range of temperature, may be separately magnified and examined.

It will be noted, by referring to Fig. 3, that when the resistance R is changed, the portion of the total temperature range to which the record sheet of ten inches in width corresponds, is shifted upward or downwards.

If the shunt resistance, S, is changed, the temperature interval to which the ten inches of record sheet corresponds may be increased or decreased. Thus, by having both R and S made variable, a cooling curve may be plotted as a whole on the paper ten inches wide, say from 900° to 0° C. or any portion of this range, as 800° to 600° C., may be spread over the width of ten inches of record sheet.

In Fig. 8, is given an actual cooling curve of a cylindrical sample of steel 6″ long by 1″ diameter, drawn with the autographic recorder in which the range is 1000° C. to 200° C. As recalescence occurs at 684° C., we wish to magnify the portion of the curve from about 750° C. to 650° C. Proper values being given to the two resistances R and S, the results were obtained which are shown in Fig. 9.

This sample of steel will be called No. 2. It had the following chemical analysis:

Carbon .97 per cent, phosphorus .035 per cent, manganese .42 per cent, sulphur .025 per cent.

We give here in Fig. 10, small portions of four curves recorded

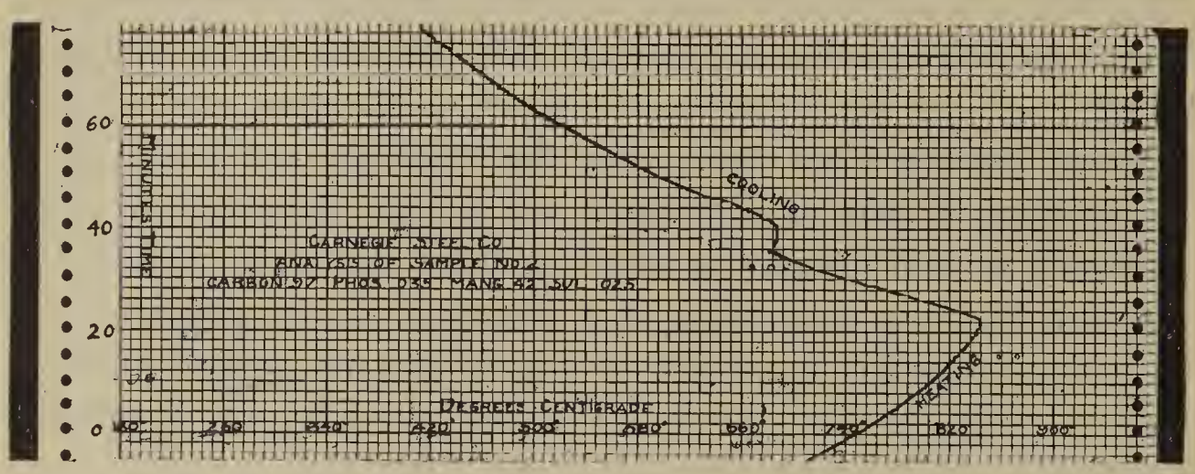


FIG. 8.
N. B. Add 18°.4 to Temperatures Shown.

at different times, using the same sample, to illustrate the precision with which the recalescence is shown to begin at the same temperature with repeated coolings when always cooled from the same temperature.

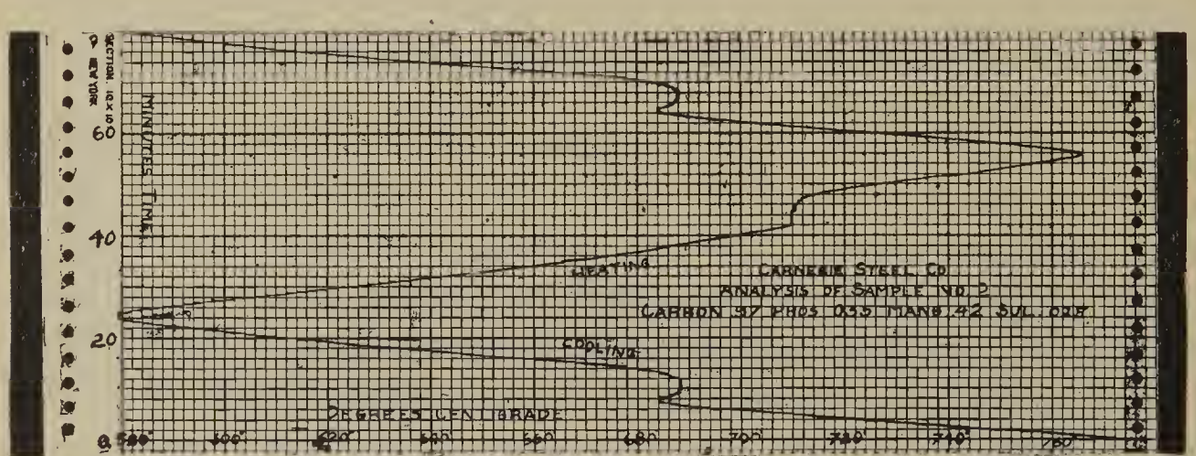


FIG. 9.
N. B. Add 18°.4 to Temperatures Shown.

The sample of steel employed was No. 2, and was cooled from 740° C. to 640° C.

It will be noted that the greatest variation of the points showing the beginning of recalescence, which occurs at 685° C. is only ¼° C. from the mean.

In Fig. 11, is given the cooling curve of sample No. 1, a low carbon steel. The recalescence point is just discernible at about

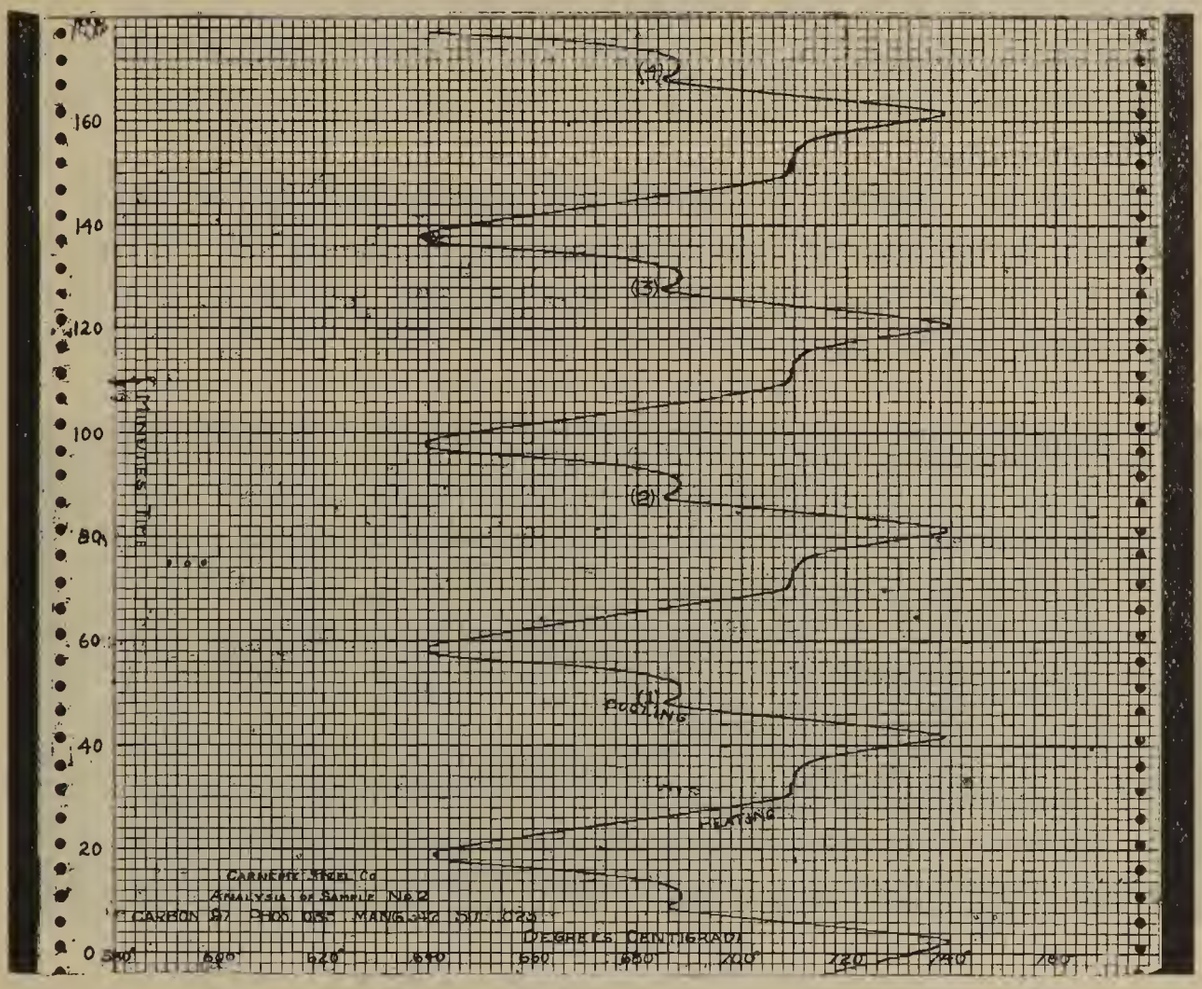


FIG. 10.
N. B. Add 18°.4 to Temperatures Shown.

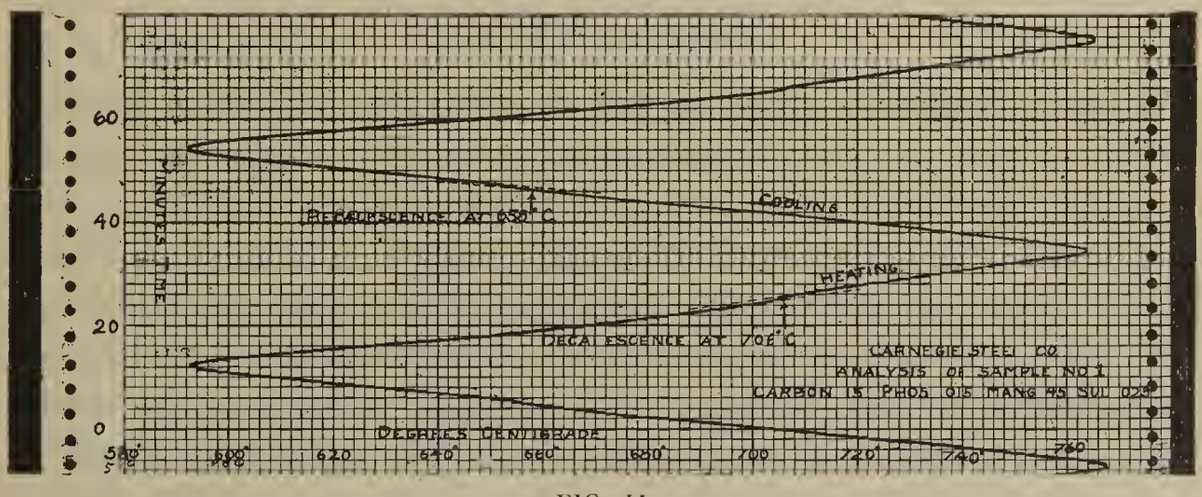


FIG. 11.
N. B. Add 18°.4 to Temperatures Shown.

658° C. The analysis of the steel gave: Carbon .15 per cent., phosphorus .015 per cent., manganese .45 per cent., sulphur .025 per cent.

Fig. 12, gives a curve of sample No. 3, a medium carbon steel. Its analysis gave: Carbon .52 per cent., phosphorus .022 per cent., manganese .60 per cent., sulphur .027 per cent.

The samples, Nos. 1, 2, 3, were six inches long and one inch in diameter and were drilled with a hole ¼ inch in diameter and 4½ inches long.

The writer wishes to express his thanks and appreciation to Mr. W. A. Bostwick, Metallurgical Engineer of the Carnegie Steel Company, who furnished the samples and their chemical analyses to the writer.

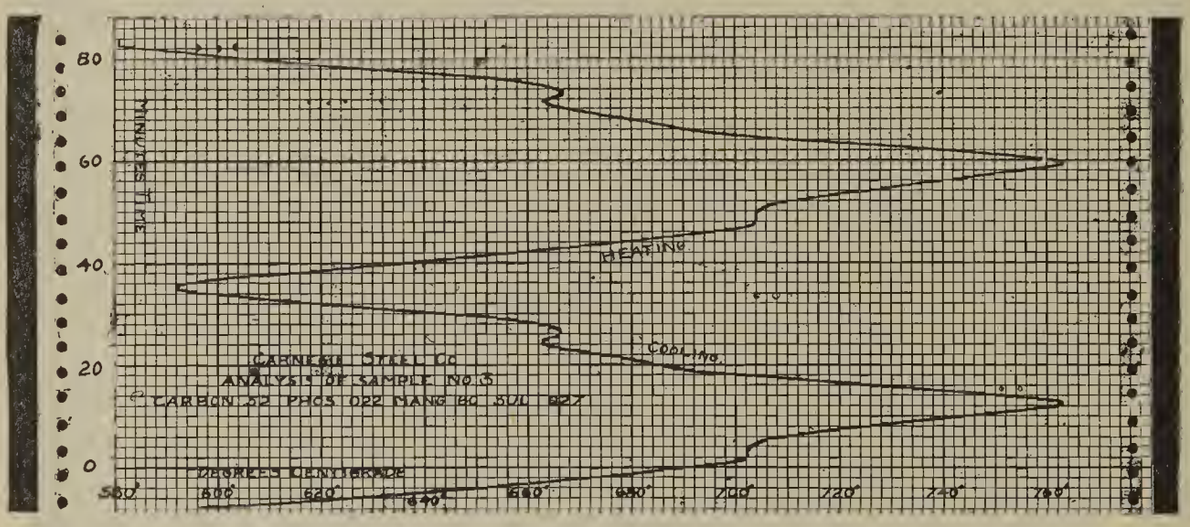


FIG. 12.
N. B. Add 18°.4 to Temperatures Shown.

Practical Suggestions For Recording Cooling Curves of Steel.

If two cylinders of great length as compared with their diameters cool under similar conditions, from the same initial temperature, the velocity of their cooling, is approximately inversely proportional to their diameters (Fourier, Analytical Theory of Heat §320). Since an autographic recorder, of any type, can keep up only with a certain maximum velocity of cooling one is limited in the smallness of the diameter of the sample which may be used. To be sure, a sample of small diameter may be cooled in an electric oven with walls insulated against loss of heat, and the heating current can be reduced for the cooling without being cut off entirely.

But, if the current is merely reduced to start the cooling, and not entirely cut off, the current which remains must be maintained

absolutely steady to avoid ambiguous results. As the result of practical tests, it was found that the diameter of the sample should lie between one-half and one inch. The recorder described above will follow the cooling of a sample one-half inch in diameter when cooled in an oven well insulated from loss of heat by a jacket of magnesia.

The recorder was arranged by means of a simple device, which it is unnecessary to describe here, to travel the pen in steps of one-forty-eighth inch when the cooling is slow, and in steps of one-twentieth inch when the cooling becomes rapid. It could thus travel the pen over ten inches in six and two-thirds minutes, a speed sufficient to follow the cooling of a sample one-half inch in diameter through the temperature range of 300° C. Samples of larger diameter, about one inch, are to be preferred. however.

The longer the sample, within limits, the better. A length of five inches was selected as giving the desired sensibility when used with a thermometer having a working resistance coil three inches in length, like that shown in Fig. 7. It was found that the diameter of the hole bored parallel to the axis of the sample was without appreciable effect on the point where recalescence began, though the subsequent shape of the inflection was modified. Holes three-sixteenths inch and one-half inch were bored in the same sample one inch in diameter, and in both cases recalescence occurred at the same temperature within less than one degree Centigrade.

It was also found that the rather delicate thermometer end (Fig. 7.) could be encased in a porcelain tube seven-sixteenths of an inch in outside diameter and give the same position of the recalescent point when inserted in a hole one-half inch in diameter, as the unencased end of one-eighth inch diameter when inserted in a hole three-sixteenths inch in diameter.

It should, however, be stated, here, that when a sample was heated to 1005° C., and cooled below the recalescent point, this point occurred at 714.5° C., but when heated to 776° C., and cooled this point occurred at 718.5° C. In other words, heating 229° higher, lowered the recalescent point 4° C.

If it is required to take the cooling curves of sheet steel, this may be done by cutting a strip five inches wide off the sheet. This strip

may be rolled up upon a half inch mandrel to form a hollow cylinder and used in the oven in the same manner as a solid cylinder with a hole bored in it.

It is important for ease of working and to obtain results, to have a properly constructed oven.

In Fig. 13 is given the design of an oven which is the outcome of a considerable experience and many trials.

The casing of the oven is made of a compound of pressed asbestos known to the trade as "asbestos wood."

The platinum heating coil is wound on the outside of a glazed porcelain tube, the winding being distributed to give uniform temperature throughout the interior of the tube. The glazing is

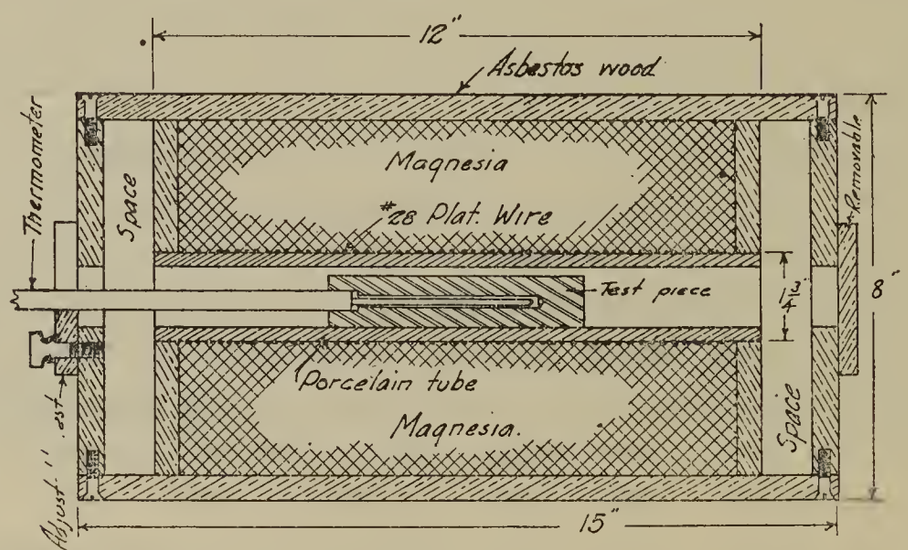


FIG. 13.

softened by high heat around the wire and retains it in place. The space around the porcelain tube is filled in loosely with powdered magnesia. The quantity of this magnesia may be varied to modify the velocity of cooling and may be removed with ease to inspect the winding or make repairs. A switch, binding posts and fuse are mounted upon the outside of the case. The winding is of No. 28 platinum wire and has 11 ohms resistance at room temperature. Extra removable pieces of asbestos wood permit the end opening to be closed tightly and yet allow the easy insertion and removal of the samples. When at full heat, the oven operates directly on 110 volts.

With the outfit of recorder, thermometer, and oven described above, many samples may be tested in a single day, and the results

obtained will be without ambiguity. Differences in the positions of the recalescent points of steel of one degree Centigrade are easily located with certainty. The curves which are drawn are drawn on thin semi-transparent cross section paper, and may be easily blueprinted for duplication. Tabulated cooling curve records of this precision accompanied with chemical analyses of the samples ought to yield information of much value in the metallurgy of steel and its protean alloys.

Philadelphia, Pa., March 18, 1909.

A paper presented at the Fifteenth General Meeting of the American Electrochemical Society, at Niagara Falls, Canada, May 7, 1909; President E. G. Acheson in the Chair.

A NEW RADIATION PYROMETER.

By Charles E. Foster.

This new radiation pyrometer is the latest development of Prof. Fery's invention in this field. It operates essentially on the same broad principle as that used in his well-known thermocouple radiation type, but with the difference that the device sensitive to heat, instead of being a thermocouple, is a multi-metallic spiral of very small dimensions. The indications of the instrument are due to the uncurling of this spiral when it is heated by the focussed radiation.

The general principle of Prof. Fery's pyrometers is probably well known. It is merely necessary in passing to refer to the main features. These can be illustrated by reference to Fig. 1. While this diagram is particularly representative of the new type, it will serve for the purpose of defining the broad action.

The radiant heat emitted by the hot body under examination is received by the concave mirror M, and brought to a focus in the little cell B. The pointing and focusing are guided by the observer looking into the eye piece E. In the little cell B are two semi-circular mirrors which reflect the focussed image of the hot body. They have on their line of junction a small circular hole through which the focussed radiation reaches the sensitive device.

In the thermocouple type of instrument this sensitive device is one junction of a very small thermocouple. The temperature measurement is then made by measuring the e.m.f., or the resulting current generated by this thermocouple. The departure in the new type is in substituting for the thermocouple a minute multi-metallic spiral. This is composed of laminæ of metals of different thermal co-efficient of expansion, thus the heating of the spiral causes it to uncurl.

One end of the spiral is mounted upon a support attached to the casing, and the other carries a very light pointer. The uncurling of the spiral is made visible and measurable by the movement of this pointer. It projects through the casing and moves over a scale carried on the instrument. It can therefore be seen that the whole thing is self-contained.

The details of the pointing and focusing arrangement are perhaps worthy of a little further explanation. Reference to Fig. 2

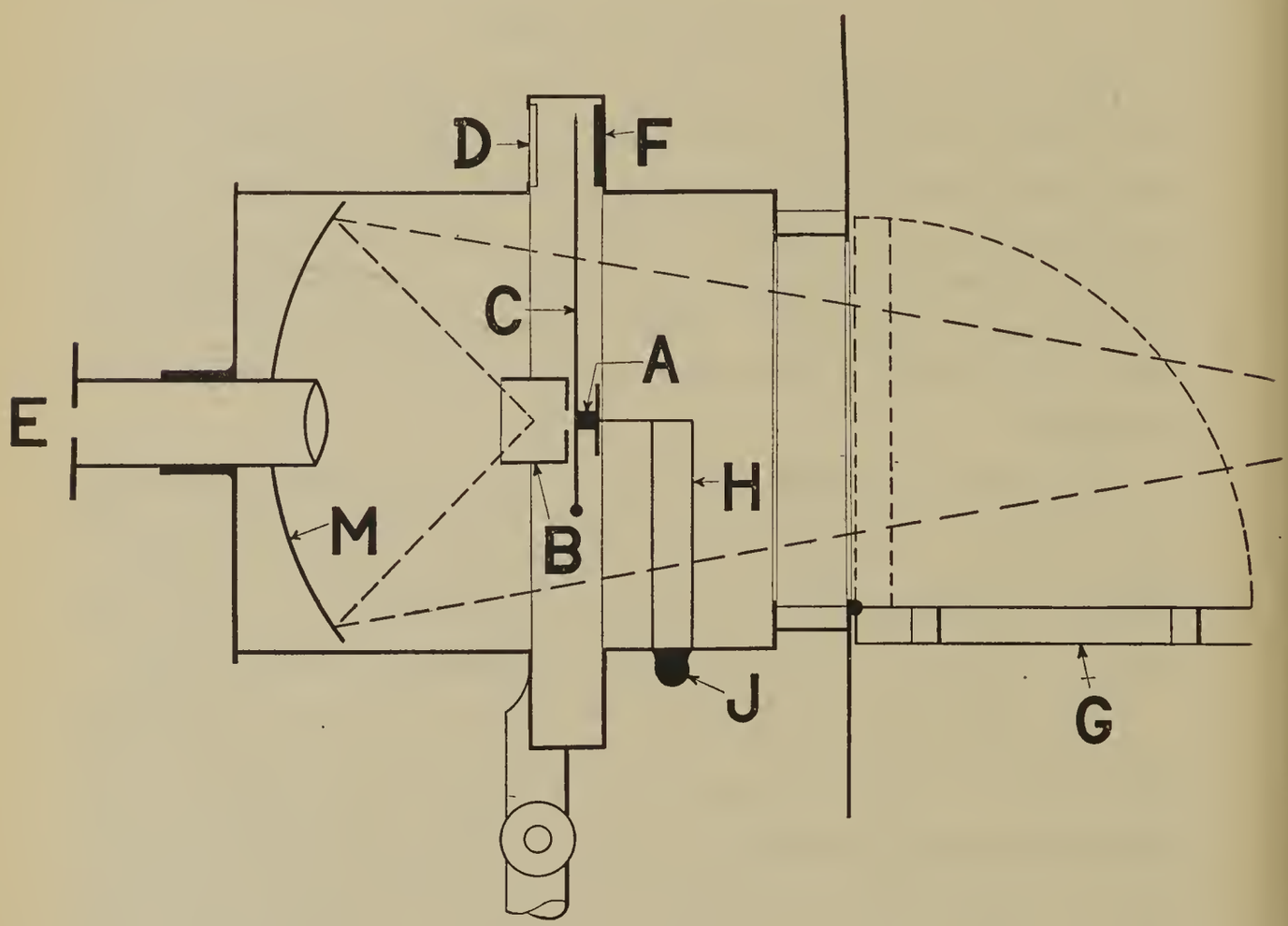


Fig. 1.

will illustrate this. In this diagram we can assume that the pyrometer is pointed at the opening of a furnace door, and the views show what will be seen through the eye-piece. In the top view the instrument is pointed centrally, but is out of focus, and it will be seen that the two mirrors have the effect of splitting the image into two portions which do not correctly match. This is achieved by setting the two mirrors at a slight angle to each other. Such an arrangement only gives a correctly joined image of the

hot body when the plane of the focus is coincident with the intersection of the two planes of these two small mirrors. The black spot in the center of the field of view is the hole through which the focused radiation reaches the sensitive device. It is therefore necessary for the observer to point the instrument so that the focussed image overlaps this black spot all round.

Fig. 3 indicates diagrammatically the arrangement of the spiral. D is the expanding portion of the spiral; at its center is fastened a small pin E of metal which is thermally a bad conductor. The

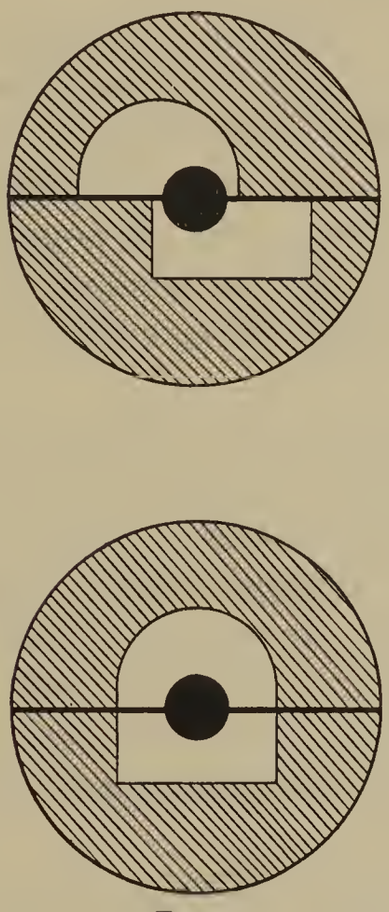


Fig. 2.

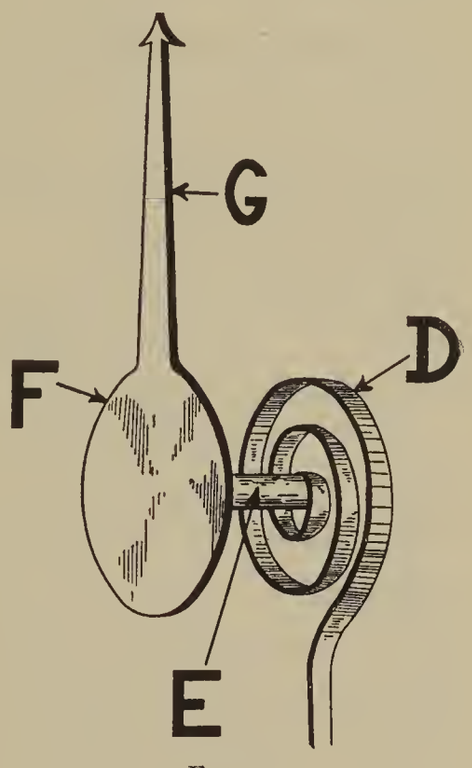


Fig. 3.

small shield F serves the double purpose of shielding the spiral from direct radiation, and of catching and throwing back such of the focussed heat rays as pass through the folds of the spiral in the first instance. The pointer G is attached to this plate. The support at the other end of the spiral is made by means of a material of low thermal conductivity, thus retaining in the spiral such heat as is focussed on to it, and preventing the rapid creep into the spiral of conducted heat from the casing.

Originally the spiral was made of two metals, but later experi-

ments showed the desirability of using three; the thermal expansion co-efficient of the intermediate metal being itself intermediate between that of the two outer metals. Those found most satisfactory are gold, plantinum and "Invar." It appears that this arrangement allows the middle metal to act as a connecting link between the two outer ones, and prevents extreme stresses at the point of junction. The total diameter of the spiral is about 1.2 mm. The fixed end of the spiral is mounted upon a support which can be moved through a small angle, in order that the pointer may be set to zero before taking a reading.

A device of this kind is of course subject to change with atmospheric temperature, and therefore provision has to be made for shielding it from any radiation while being set to zero. This is illustrated by the shield G in Fig. 1. The dotted outline shows its position when setting the spiral to zero. C is the pointer moving over the scale F and viewed through the window D. The fixed support H is moved circumferentially by the knob J working in a slot in the casing.

The directions for using the instrument are extremely simple, being first to set the pointer to zero with the instrument closed; then open the shutter and sight the pyrometer by means of the eye piece. This being done, watch the pointer until it reaches a steady reading, which will be in about 20 seconds. This steady reading is then the black body temperature of the hot body under examination. Of course there will be a slow after-creep of the pointer due to the general heating up of the instrument, but this must be ignored in taking the reading.

While for many purposes the electrical method will be preferable, it is believed that as a self-contained instrument this new spiral type of radiation pyrometer will have many applications.

DISCUSSION.

Mr. Henry Howard: I would like to ask what effect the distance of the object that you are measuring the temperature of has on the readings, that is, the distance from the apparatus to the heated object.

MR. C. E. FOSTER: The distance is a matter of no moment, provided you cover the aperture, or black spot (see Fig. 2), with the image of the hot body. That is a geometrical result of the arrangement. Assuming that you have first focussed it at such a distance that your image just overlaps the black spot—then suppose you go to half that distance—as a geometrical result the diameter of the focussed image will be twice what it was before. The angle subtended by the concave mirror will also be twice the previous diameter. Therefore you would receive four times the amount of radiation; you spread it over four times the area, leaving the intensity the same. But since you have limited the amount of radiation which reaches the thermo-couple, that makes no difference in the reading.

MR. HOWARD: How rapidly a fluctuating temperature can you follow?

MR. FOSTER: The time of reading the temperature is about twenty seconds so that you could probably take a different reading at intervals of thirty seconds. That would be about it.

MR. W. H. BROWNE: I would like to ask Mr. Foster what is the range and accuracy claimed for the readings?

MR. FOSTER: The range is anything you like to make it. It is perfectly flexible in the upward direction, because all you have to do if the range is not high enough is to reduce the amount of radiation that reaches your mirror from the hot body. Then it takes more to reach a convenient angle of deflection. Downward, the smallest deflection in this instrument is 500 C. It is not supposed that you could use it down there. Possibly 600 or 700 is about the lowest limit for definite work. So the accuracy, we claim, would be, say, within 2 per cent. at 1,000 and over. It is rather early to give a definite figure. The calibration of this instrument shows it is well within 2 per cent. at 1,000 C. and above, but we may probably increase it considerably. It is rather new to know what our limits of accuracy are. Roughly, 2 per cent. at 1,000 C.

MR. BROWNE: Another question in regard to the constancy of the calibration: Have you any figures on that yet?

MR. FOSTER: We have none beyond the original tests in this design. It is rather new, so that it is difficult to say at this day. It holds up to its calibration very well so far.

MR. L. E. SAUNDERS: I would like to ask, in ordinary work what distance from the object is it necessary to set the instrument, and how small an aperture is it possible to sight into?

MR. FOSTER: The general angle of the cone is about 30 to 1. That is, your distance must not exceed 30 times the diameter of the hot body, whatever it is. Of course, there is no limit in the other direction. That is, at a 1-inch peep-hole you would have to come within 30 inches, and so on.

MR. C. A. HANSEN: Mr. Chairman, I have had more or less experience with the original type of Fery pyrometer, and have a few criticisms to make. In the first place, unless the ratio of the radiant energy incident upon the mirror to the radiant energy reflected from the mirror to the sensitive device is constant, the instrument will not give satisfactory results. This ratio can only remain constant if the mirror surface remains bright, and it does not remain bright long in an average laboratory, according to my experience. This criticism would apply to the present form of instrument. The two other criticisms I wish to make concern the millivolt meter furnished with the earlier instruments. The suspension of the movable coil in this meter was a long, spraddly, bronze spring, so easily disarranged that it was almost impossible to get two consecutive equal deflections with the same e.m.f. actually impressed. Again, the magnet and movable coil were coated with some magnetic lacquer that scaled off and, arranging itself in the direction of the magnetic flux, naturally interfered seriously with the rotation of the coil. Taking it altogether, my experience with the instrument was decidedly unsatisfactory.

On the other hand, comparing it with the Wanner pyrometer, the only other type of "optical" pyrometer with which I am familiar, I thought the Fery might be developed into the more convenient instrument. When sighting at intensely hot bodies with a Wanner, it is almost always necessary to direct the pyrometer by sighting along the top of the tube. The eye is dazzled by the white light, and it is difficult to adjust the eye to the red light actually made use of by the instrument. This fault is not inherent in the Fery. Another point in favor of the Fery, as compared with the Wanner, is the direct reading scale characteristic of the former.

PROF. J. W. RICHARDS: The great advantage of this type of pyrometer for general use is that there is nothing to go in the furnace and nothing to wear out. That is an exceedingly important thing. I have yet to find the instrument which goes in the furnace that is not quickly deteriorated by use, whereas these are worn out no more than is a pair of spectacles by looking through them.

PROF. S. A. TUCKER: As to which of the two pyrometers, Fery or Wanner, is best to use, I have used both, but have used the Wanner considerably more than the Fery. The Wanner has one great advantage in being applicable to a very small aperture, which makes it more useful in small electric furnaces. As to the difficulty from the eyes being dazzled, after you have had some practice with the Wanner the field can usually be explored through the instrument; the hottest part is thus found by the increase in the intensity of the red light.

MR. S. E. HITT: I would like to ask, in case you want to get the temperature of the bath in an open hearth furnace, what effect the hot gases over the bath would have with this instrument; in other words, if a correction could be made for the gases, giving a fairly accurate temperature for the bath?

With reference to measuring the temperature of metal in the open hearth you have this difficulty. You have slag on top, and all you can do is measure the temperature of the slag. You cannot see the steel itself unless you sink a fire-clay tube into the bath and sight into the bottom of that fire-clay tube. As a matter of fact, a very good way is to sight upon the slag, because with the standard practice you can work by the temperature of the slag quite easily.

MR. HOWARD: I would like to ask if the temperature of the apparatus remains constant, whether that crawling effect would exist, or whether the apparatus would continuously give an accurate reading of the temperature.

MR. FOSTER: The crawling effect will exist just so long as there is a temperature gradient in the instrument, that is, until it reaches a final temperature. Generally you take it from a cool place into a hot furnace room, and it will gradually creep up; but you can set the pointer every time at zero before you take the reading.

MR. HOWARD: I was wondering, if you wanted a continuous reading from the apparatus, if it was fixed permanently.

MR. FOSTER: No, you must take isolated readings. You couldn't get continuous readings from that instrument.

MR. HOWARD: Not even if it was water-cooled?

MR. FOSTER: The dimensions of the spiral are about 1.2 mm. in diameter over the whole spiral, so that one couldn't water-cool it very well.

In reference to the question of the detail design of the Fery thermo-electric pyrometer, I am happy to say that it has been very much improved recently. We recognized all those difficulties which were inherent in the original instrument, and we have been working hard here in the States to remedy those, and we have now got to the point that we are using a double-pivoted movement. There is no suspension at all, strictly speaking, in the indicator. We are using a higher efficiency, and as a result we get rather more e.m.f. when the pyrometer is sighted at a hot body at 1,300 C. than if you would put a Le Chatelier couple into 1,300; so that we get a high resistance indicator, with a couple of greater e.m.f., and no suspension. Therefore, we have got that point dealt with satisfactorily.

As far as the mirror is concerned, that is gilded on the face, and then the glass is made to absorb the gold to a certain extent, so as to hold it tightly. Then you have three points to bear in mind in connection with any possible clouding of the mirror. The first is that it is easily washed; the next is that it works upon the Stefan-Boltzman law of radiation. If you put it in a rough way, 1 per cent. decrease in the reflecting efficiency of the mirror will only make ¼ per cent. error in temperature. Another point is that the clouding of the mirror is less likely to affect the long wave lengths with which the pyrometer works than the short wave lengths of the visible light.

A paper presented at the Fifteenth General Meeting of the American Electrochemical Society, at Niagara Falls, Canada, May 8, 1909; President E. G. Acheson in the Chair.

OBSERVATIONS ON ALLOYS OF ELECTROLYTIC IRON WITH ARSENIC AND BISMUTH.

By Charles F. Burgess and James Aston.

It has been noted that the presence of arsenic in acid pickling solutions causes a marked diminution in the rate of attack by the acid, and the idea was suggested that if the presence of arsenic in a corrosive solution protected iron from corrosion by that solution, that the presence of arsenic in the iron itself might increase its durability. To test this possibility, such alloys were made, but they failed to show any marked advantage over iron and steel of ordinary grades in their ability to resist corrosion. From the arsenic alloys prepared primarily for this purpose, test bars were made and subjected to the various physical tests to which a large number of other alloys have been subjected in an extensive investigation on the properties of alloys made from electrolytic iron.

In this investigation, which has been made possible through a grant from the Carnegie Institution of Washington, some six hundred ingots of iron and iron alloys have been made, and from these about five hundred forged bars have been secured, these bars covering a considerable range of composition, over half of which are binary alloys.

In determining the magnetic properties of the arsenic alloys, some interesting and unexpected results were obtained, which in turn suggested the advisability of testing the influence of the analogous elements, antimony and bismuth, upon the magnetic quality of iron.

While the tests on these alloys are incomplete, being still in progress, and although the data is not sufficiently complete and extensive to warrant the derivation of positive deductions, the results of this work are given as showing the desirability of further investigation along this line.

The general idea upon which our investigation on iron alloys

has been based is that comparatively little is known of the properties of iron alloys free from carbon, and, that the production and study of such alloys appears to offer an interesting field of work. The iron which has been used for this purpose is that which has been electrolytically refined from Swedish iron bars and this subsequently melted and then forged into bars of as high a purity as possible.

Some idea as to the purity of electrolytically deposited iron which has been employed may be taken from the following table, giving the results of analyses reported by Messrs. Booth, Garrett & Blair, of Philadelphia.

TABLE I.

	Single Refined.	Double Refined.
Sulphur	0.001	None
Silicon	0.003	0.013
Phosphorus	0.020	0.004
Manganese	None	None
Carbon	0.013	0.012
	0.037	0.029
Iron (difference)	99.963	99.971
Hydrogen	0.083	0.072

This material has been melted alone or with the desired alloying elements in an electric furnace using granulated carbon resistor material into which is embedded magnesia crucibles containing the charges, the crucibles being removed from the furnace after cooling. Special attention was given to preventing contamination of the crucible contents, by using dense electrically shrunk magnesia crucibles with a magnesia cover, and the crucibles in turn being placed in an Acheson graphite crucible with a graphite cover.

The atmosphere under which the melting takes place is one composed mainly of nitrogen and carbon monoxide, and that this atmosphere is not without influence in contaminating the molten charge is shown by the fact that subsequent analysis reveals a slight increase in the amount of carbon. This probably comes about through a reversible action, as indicated by the equation

$$Fe + CO = FeO + C.$$

Various analyses show that this increase in the amount of carbon is probably not more than 0.04 per cent. In the subsequent

forging of the ingots into bars 20″ long x 5/8″ diameter, very little impurity is imparted to the bar.

In general, the ingots weigh about 500 grams, and the bars produced from them have been subjected to various tests for properties, and mainly those which do not destroy the bars during the process of testing. The determinations of the magnetic properties, including permeability, coercive force, retentivity and the measurement of electrical resistance, have received special attention, while comparatively few tests have been made upon tensile strength.

Among the various instruments available for testing the magnetic properties of iron, that designed by Professor Esterline has been adopted, and this after an investigation of the merits of the various methods had been made. The reasons for adopting the Esterline instrument lie in its ability to accurately reproduce results, in its ease and rapidity of working, and in the convenient form of sample test bar which it requires. The test bars are about 20 cm. long and 1 cm. in diameter. The Esterline instrument which was used was specially designed to meet our requirements. While the method employed in this instrument gives comparative results, we believe that it may be calibrated with such accuracy that the results may be as dependable as those secured in the ballistic-ring method. While the results which we obtained with this instrument may not necessarily be strictly comparable to results obtained by others using different methods, we are convinced that all data which we have secured is comparable in itself.

Comparatively little attention seems to have been given to the influence of arsenic on iron beyond the influence of the slight quantity of arsenic which may be met with in commercial iron. The work of Harbord and Tucker (Iron & Steel Institute, 1888, Vol. I); of Stead (Iron & St. Inst., Vol. I), and of Marchel (Bul. Soc. d'Encour, 1899), covers the mechanical properties exclusively, the general conclusions being that small percentages of arsenic not exceeding 0.20 per cent. have no material effect on the strength. Larger amounts result in the brittle material, but the hot working is not affected, even with 4 per cent. of arsenic. Friedrich's investigation (Metallurgie, 1907) is entirely a metal-

lographic study, and shows that arsenic alloys with iron in all proportions up to 56 per cent., under his conditions of mixing.

The method employed in making the arsenic alloys was to place the arsenic, together with the iron, in the magnesia crucible and melt in the ordinary manner. Attempts have been made to produce alloys in various proportions up to 10 per cent. of arsenic. Subsequent analyses, however, showed that the maximum amount of arsenic taken up and retained by the iron was about 4 per cent. In addition to the alloys of arsenic with pure iron, alloys were made up adding 5 per cent. of arsenic to a high grade commercial transformer iron. Table II gives the series of arsenic-iron alloys which have thus been produced. This table shows the incompleteness of our data, in that check analyses have not as yet been obtained by quantitative analysis to show the probable amount of arsenic contained in those samples where the analysis is still lacking.

TABLE II—ELECTROLYTIC IRON.

Bar No.	Per cent. Arsenic By Mixture	Per cent. Arsenic By Analysis	Per cent. Carbon	Remarks
117 A	0.00	0.000	0.047	
121 I	0.25	0.292		
121 H	0.50	0.430		
113 A	1.00	0.915		
113 B	2.00	1.810	0.042	
113 D	4.00	3.862		
113 F	6.00	4.141		Broken—not tested quenched.
113 H	10.00	3.563		
92 A	1.00	.....		Tested only in unannealed state, not yet complete.
113 C	3.00	.....		
113 E	5.00	.....		
171 L	4.00	.....		Tested unannealed and lost in annealing.
172 B	5.00	.....		Twice annealed but not quenched.
		Commercial Transformer Iron.		
171 O	0.00..	.....		Tested unannealed, lost in annealing.
171 P	5.00%			
172 C	0.00..	.....		Twice annealed, not quenched.
172 D	5.00%			

It has been found that all the arsenic ingots forged readily under normal forging temperatures. The odor of arsenic was very evident upon heating, even at the low temperatures pro-

duced by grinding, and this alliaceous odor was very intense during the forging.

It is evident from the analyses that under conditions of working, 4 per cent. of arsenic is about the maximum that may be counted upon, and below this percentage the arsenic is taken up in about the percentages calculated, showing no great loss by volatilization.

The forged bars of 20″ in length were cut into three test bars, two for tensile tests and one for the magnetic tests. The tensile bars were about 5″ long, and turned down over a clear length of 2 inches to about 0.4″ diameter. The tests were made in a Riehle 1,000,000 pound testing machine. No special difficulty was noticed in machining the bars, the higher arsenic seeming to be brittle, which brittleness is also confirmed by the following data on strength.

TABLE III—STRENGTH TEST.

Arsenic Alloys.

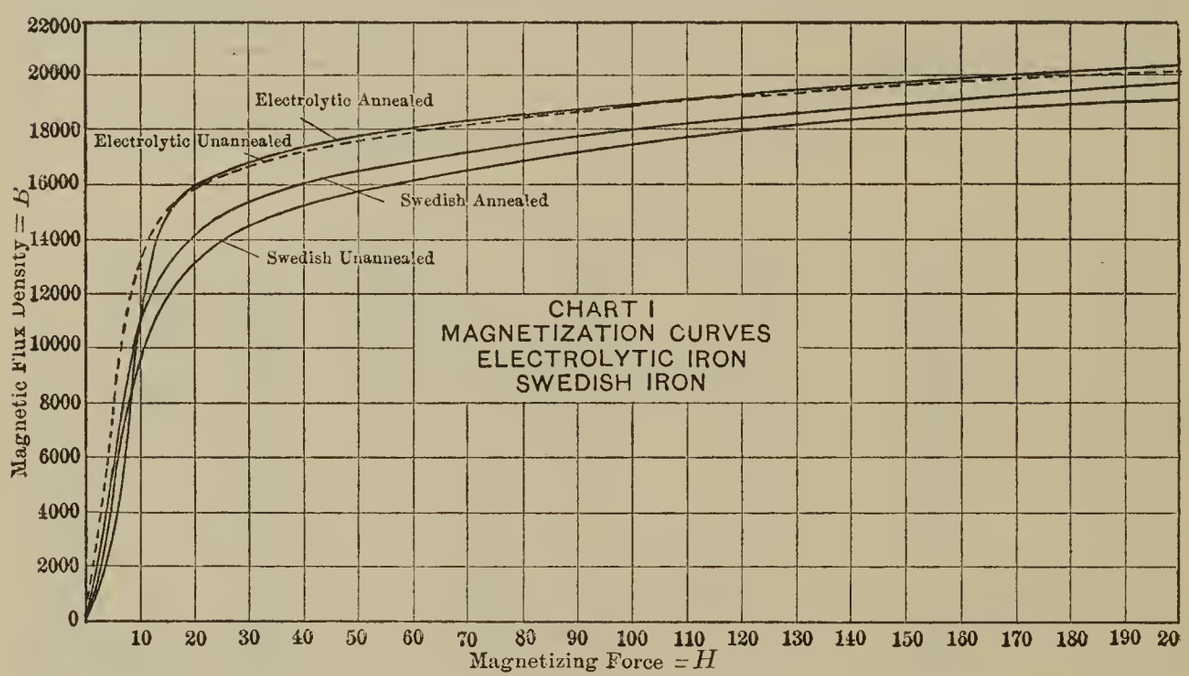
Bar No.	Per cent. Arsenic	Stress in $^{\#}/_{\square}$ Ultimate	Stress in $^{\#}/_{\square}$ Elastic limit	Per cent. Elongation	Per cent. Reduction of area	
121 I	0.292	61,250	47,900	27.5	68.2	(flaw)
121 A	0.430	65,500	53,000	28.5	58.3	
113 A	0.915		47,000			(flaw)
113 B	1.810	60,250	53,500	0.0	3.7	
113 D	3.862	63,900	63,900	1.0	1.7	
113 F	4.141					
113 H	3,563	61,250	61,250	1.0	0.65	
		Electrolytic Iron.				
117 A	Elec. forg.	50,000	40,000	31.0	91.4	(greatest reduction of area.)

MAGNETIC TESTS.

The magnetic tests consisted in general of a magnetization curve and readings of the retentivity and coercive force for each bar, after being subjected to each of four different heat treatments; first, as forged; second, after heating to 675° C. and slowly cooling; third, after heating to 1000° C. and slowly cooling; fourth, after heating to 900° C. and quenching in water. All the heating was done in the electric resistor furnace, and the bars were packed in ground magnesia, in a magnesia-lined graphite box. The temperature readings were taken with a thermo-couple. The heating and cooling proceeded very slowly,

in general about three to four hours being required to bring the temperature to the desired point; it was then held constant for one to two hours; after this the bars were allowed to cool in the furnace, about twelve hours being necessary for a temperature drop to 200° or 300° C.

We have taken as a reference standard an electrolytic iron bar No. 117 A, in its unannealed condition, since among the earlier tests on electrolytic iron this sample reached the highest maximum of magnetic density, and showed great uniformity throughout the length of the curve, having a steep slope in the early part of the curve, but a gradual bend as saturation was approached; also because annealing had little influence on the quality of this bar. The quality of this bar is indicated in Chart



I, and in the accompanying Table IV, in which the magnetic flux density of this electrolytic material for different applied magnetizing forces is compared with a sample made from our Swedish anode bars, and which is representative of a good quality of wrought iron, as may also be seen from Table IV, where comparative figures are given for Hopkinson's classic wrought iron sample, formerly a standard of magnetic excellence.

TABLE IV.

No.	Comp.	H = 10	H = 20	H = 50	H = 100
117 A	Electro. forged unannealed	13,100	15,750	17,600	18,850
NWS	Swedish anode. unannealed	9,500	13,200	15,700	17,450
	Swedish anode. annealed 675	10,000	14,200	16,500	18,000
Hopkinson's Wrought Iron		10,300	13,950	15,650	16,500

TABLE V—MAGNETIC TESTS DATA.

Bar	Comp. Per cent.	H = 10				H = 20				H = 50				H = 100			
		Unann'd	Ann'd 675	Ann'd 1000	Quench 900	Unann'd	Ann'd 675	Ann'd 1000	Quench 900	Unann'd	Ann'd 675	Ann'd 1000	Quench 900	Unann'd	Ann'd 675	Ann'd 1000	Quench 900
Iron																	
NSW	Anode	9,500	10,000	10,850	8,400	13,200	14,200	13,900	12,050	15,700	16,500	15,850	15,550	17,450	18,000	17,200	17,100
117 A	Elec. Forged	13,100	10,000	13,350	11,800	15,750	15,950	15,450	14,600	17,600	17,700	17,050	16,950	18,850	18,850	18,200	18,150
Antimony																	
172 E	1.15	8,800	10,000	7,700	. . .	12,800	13,350	11,600	. . .	15,300	15,750	14,800	. . .	16,950	17,100	16,400	. . .
Arsenic																	
121 I	0.29	10,500	13,200	10,800	11,200	14,750	15,550	14,100	14,750	16,900	17,250	16,500	16,700	18,350	18,550	17,850	17,950
121 H	0.43	7,000	7,800	10,400	8,100	13,000	14,000	13,750	12,750	16,300	16,600	15,950	16,250	17,800	18,100	17,250	17,600
113 A	0.[illegible]	6,200	6,250	11,950	12,600	13,200	14,050	14,750	15,300	16,450	17,000	16,650	17,050	17,950	18,550	17,950	18,250
113 B	1.81	8,300	11,850	12,600	10,300	13,950	15,750	15,150	13,800	16,700	17,450	16,850	16,650	17,950	18,750	18,150	18,250
113 D	3.86	13,850	15,050	14,850	13,600	15,350	16,300	15,750	15,450	16,450	17,550	16,850	16,900	17,600	18,650	17,850	18,100
113 F	4.14	13,300	14,200	14,650	. . .	15,500	15,900	15,750	. . .	17,000	17,250	17,050	. . .	18,200	18,450	18,150	. . .
113 H	3.56	12,400	14,200	12,300	13,450	15,000	16,100	14,600	15,450	16,700	17,550	16,650	16,900	17,950	18,750	17,950	18,000
Bismuth																	
172 G	1.0	7,000	11,550	6,300	. .	13,250	14,650	11,350	. . .	16,800	16,850	15,500	. . .	18,600	18,350	17,550	. . .
172 H	2.0	9,200	13,250	9,700	. . .	15,500	16,100	12,750	. . .	18,350	18,350	16,050	. . .	19,650	19,750	17,800	. . .
172 J	4.0	7,700	10,500	10,000	. . .	12,600	13,750	13,500	. . .	16,250	16,550	16,650	. . .	18,050	18,050	18,350	. . .
172 K	6.0	9,100	12,000	6,400	. . .	13,250	14,700	12,950	. . .	16,650	16,850	16,250	. . .	18,350	18,100	18,250	. . .
172 L	10.0	6,100	9,500	7,750	. . .	12,000	13,200	11,050	. . .	15,800	15,800	14,850	. . .	17,600	17,350	17,450	. . .
Special																	
172 C	Trans.	6,500	9,550	8,600	. . .	12,050	13,550	12,400	. . .	15,850	16,550	15,850	. . .	17,700	18,050	17,450	. . .
172 D	+ 5 AS	9,100	11,500	8,500	. . .	13,700	14,750	11,800	. . .	16,500	16,750	15,300	. .	17,950	18,000	16,950	. . .

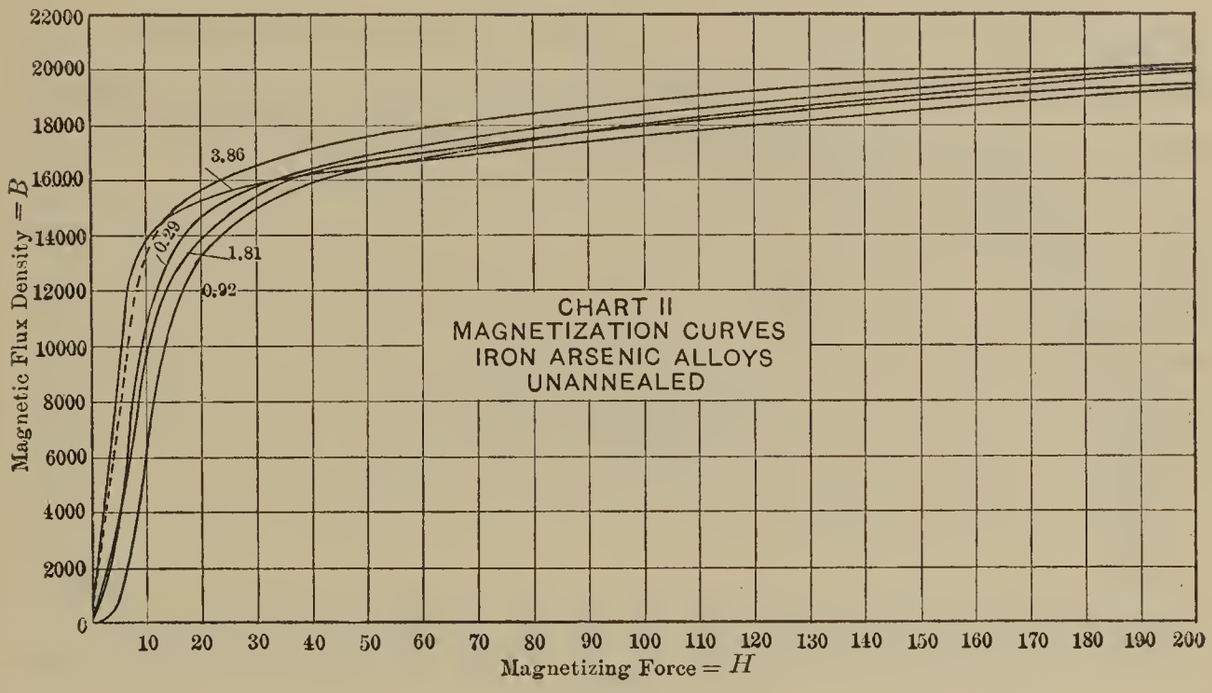
This standard reference curve for electrolytic iron is indicated in all drawings by a dotted curve. It does not represent the ultimate standard of quality of pure iron, since we have in our later tests found samples of electrolytic iron of presumably higher purity, which have shown somewhat higher magnetic qualities, but it is satisfactory as a standard reference curve in showing that if the alloys approach this curve they have exceptional magnetic qualities.

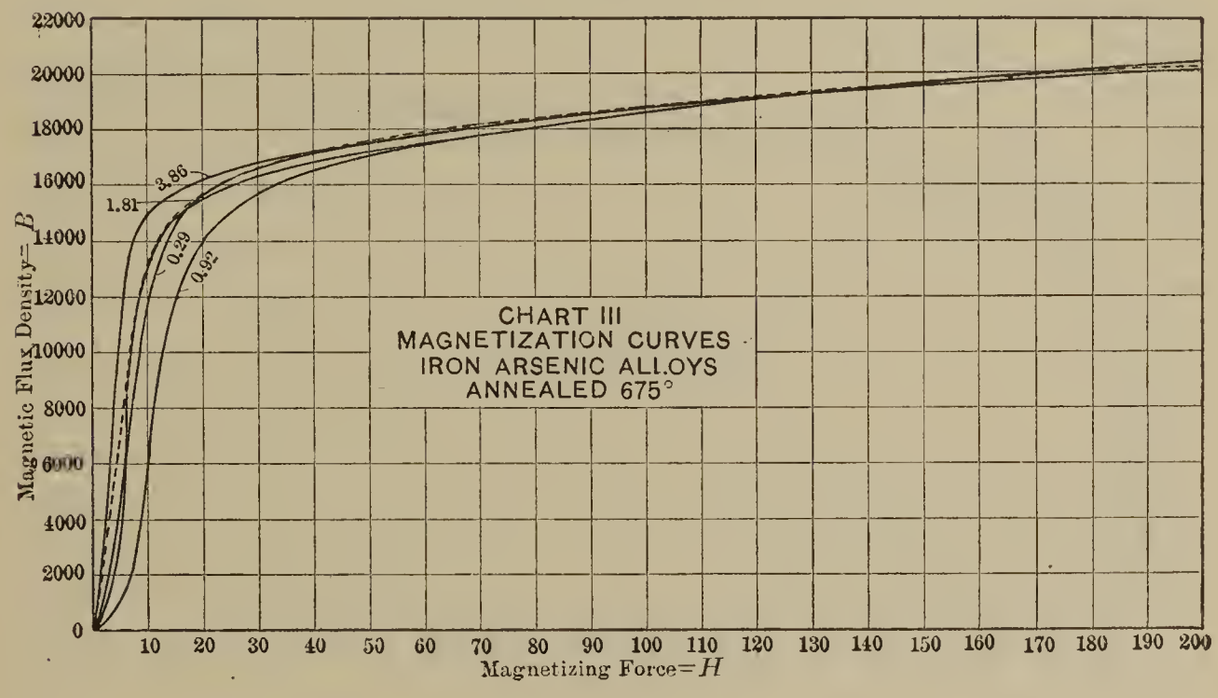
As is shown by Table II, magnetic tests have not been completed for all of the various heat treatments; also a few bars were lost by breakage and in annealing. It is also the intention to make additional series of similar alloys for further confirmatory tests, but the results as far as completed at the present time are given in the accompanying tables and curves.

TABLE VI—COERCIVE FORCE AND RETENTIVITY.

Bar	Comp. Per cent.	H (Max) = 200 COERCIVE FORCE				H (Max) = 200 RETENTIVITY			
		Unann'd	Ann'd 675	Ann'd 1000	Quench 900	Unann'd	Ann'd 675	Ann d 1000	Quench 900
Iron									
NSW	Anode	5 5	4.8	3.9	5.0	11,400	12,700	9,000	8,500
117 A	Elec. Forged	5.5	6.2	3.1	2.5	12,300	13,800	10,000	8,000
Antimony									
172 E	1.15	7.3	5.0	4.0	. . .	12,000	8,700	6,900	. . .
Arsenic									
121 I	0.29	6.5	5.5	4.5	4.0	12,400	14,600	9,900	10,800
121 H	0.43	8.2	8.0	5 5	4.3	12,700	12,700	9,400	8,600
113 A	0.92	9.5	9.2	5.3	3.0	12,700	14,700	12,300	9,500
113 B	1.81	5.9	5.0	3 7	3.0	10,300	12,200	8,900	8,600
113 D	3.86	4.0	3.5	2.0	2.1	12,100	13,000	6,500	8,600
113 F	4.14	5.0	3.3	2 3	. . .	10,800	12,300	8,900	. . .
113 H	3.56	4.5	4.0	2.7	2.7	11,000	13,400	8,600	8,900
Bismuth									
172 G	1.0	8.3	4.6	7.3	. . .	12,900	10,800	10,300	. . .
172 H	2.0	7.0	4.2	4.5	. . .	13,200	11,000	8,500	. . .
172 J	4.0	8.0	5.0	4.3	. . .	12,200	11,200	7,600	. . .
172 K	6.0	7.5	3.9	6.2	. . .	12,400	9,700	10,800	. . .
172 L	10.00	8.7	5.0	4.7	. . .	12,900	10,300	8,900	. . .
Special									
172 C	Trans.	8.1	6.2	4.5	. . .	11,100	12,300	8,700	. . .
172 D	+ 5 AS	6.6	4.0	3.9	. . .	12,600	11,500	7,900	. . .

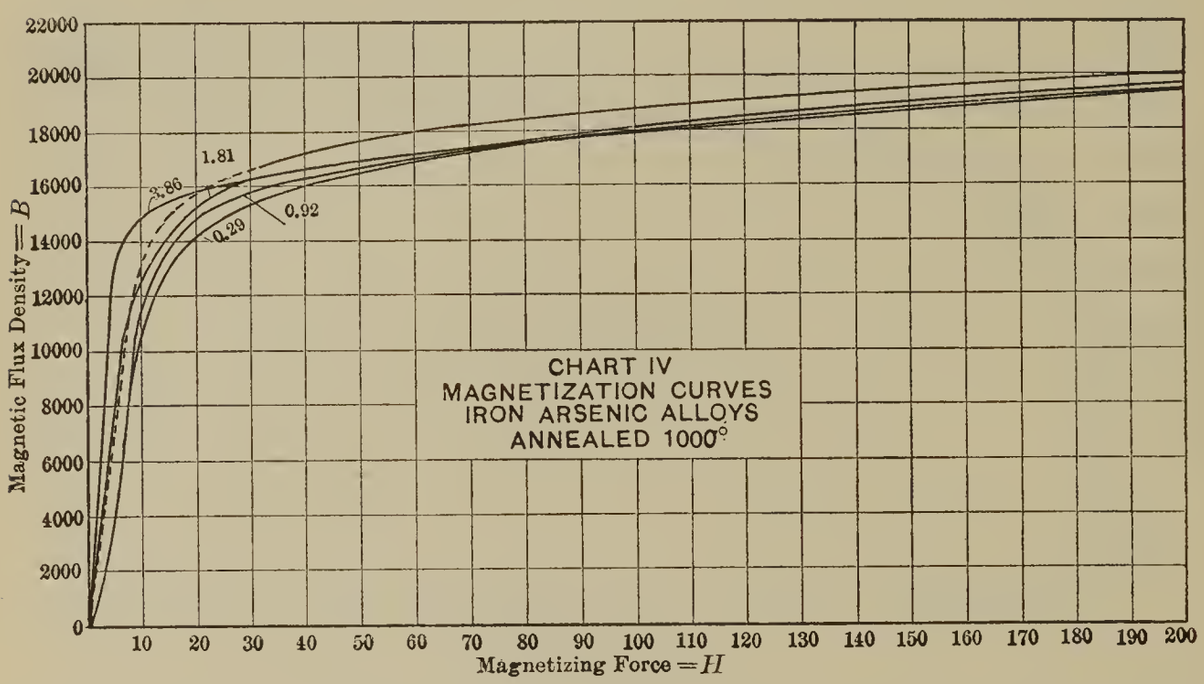
Magnetization curves for representative bars are plotted in Charts II, III, IV and V, and the data for comparison in Tables V and VI. For the lower values of the arsenic content there is nothing of particular interest. Bar 121 I, with arsenic content

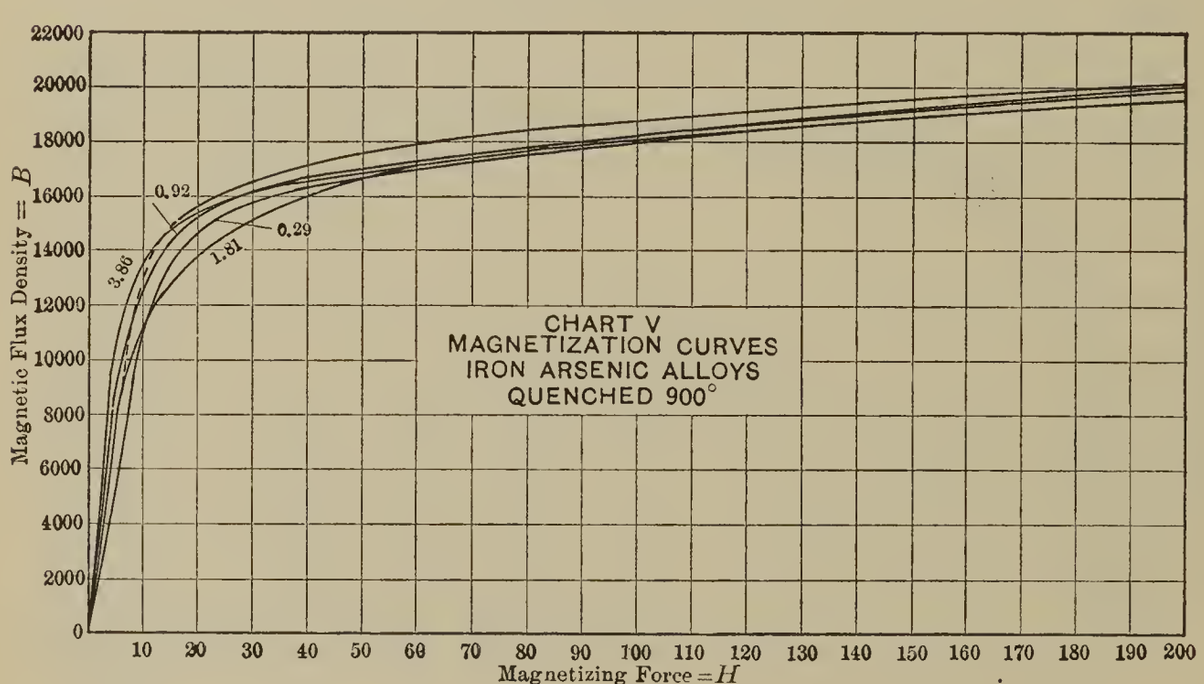




of 0.29 per cent. is very close to the standard electrolytic curve; bars 121 H and 113 A with 0.43 per cent. and 0.915 per cent., respectively, are poorer in quality. This is shown also in the relative coercive forces of 6.5, 8.2 and 9.5 for the unannealed state. Further increase of arsenic to 1.810 per cent in Bar 113

B shows an improvement in quality, and the coercive force has dropped to 5.9. But the most interesting features are noted with the higher arsenic alloys 113 D, 113 F and 113 H, with 3.862 per cent., 4.141 per cent. and 3.563 per cent. respectively. For lower





values of the magnetizing force, the density reaches very high values for relatively small impressed field, being for 113 D and 113 F considerably higher than in the case of our electrolytic iron 117 A. The coercive forces also are the smallest noted in any of our tests of the unannealed bars, being 4.0, 5.0 and 4.5.

When H reaches 20, however, the curves fall below that of the electrolytic iron in the unannealed condition.

The effect of successive heat treatments is seen by inspection of the curves and tables. A marked improvement throughout the entire range of the curves is the result of heating to 675° C. and slowly cooling, due, no doubt, to the removal of all forging strains and the opportunity afforded for the grain size of the material to become normal; this improvement of the already good results observed place the arsenic alloys on an equality with the best electrolytic material for magnetizing forces, above H = 50, and below this value of H they are considerably superior, thus ranking with the very best magnetic material for which records are available. Comparing 117 A and 113 D, both annealed at 675° C, we note densities of 10,000 and 15,050 for H = 10, and for H = 20, the values are 15,950 and 16,300, respectively. At H = 50 the densities are practically equal, being 17,700 and 17,550.

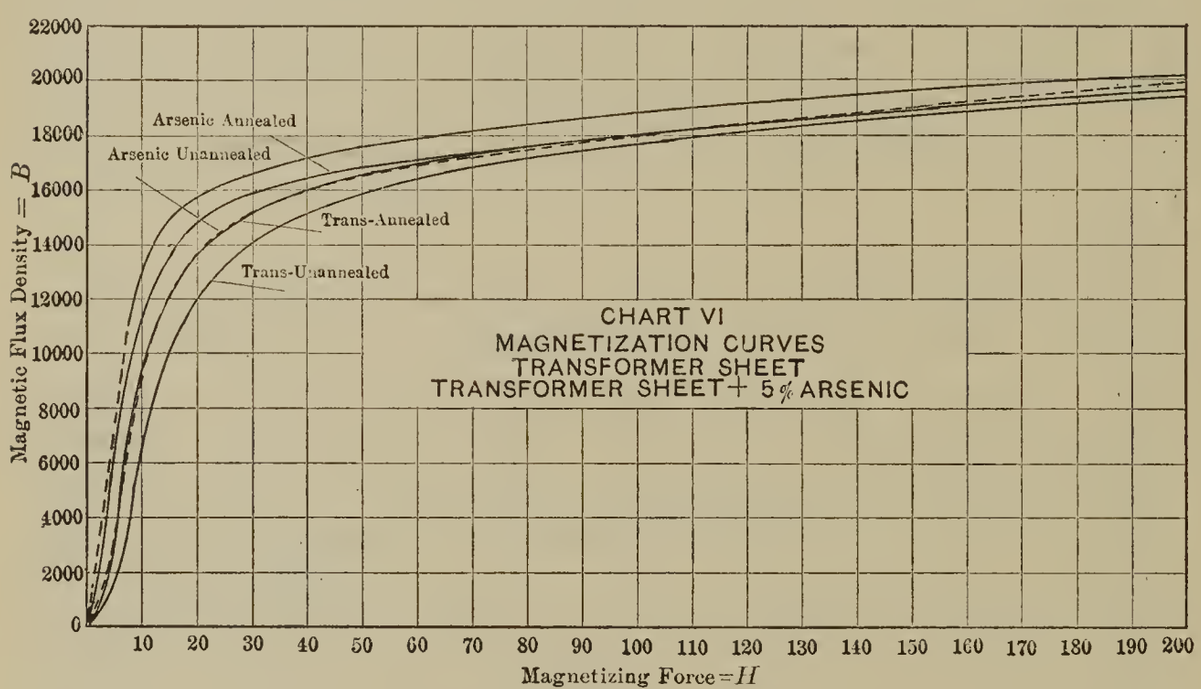
The second heating to 1000° C with slow cooling in general has been accompanied by an improvement of the quality in the lower ranges of the magnetizing forces, but there is a decided falling off throughout the upper ranges of the curve. Quenching from 900° C shows no hardening, there being but slight changes in the magnetization curves. Referring to Table VI, the tabulation of the coercive forces shows a continual falling off after successive heatings, and even after quenching. The low values of coercive force for the higher arsenic content are worthy of note, the mininum of 2.0 being reached by 113 D with 3.86 per cent. after annealing at 1000° C.

The retentivity data allows no deductions to be drawn. In general, it varies with the maximums attained by the magnetization curve increasing as the usual accompaniment of annealing at 675° and decreasing after a 1000° heating and after quenching.

To determine the effect of the addition of arsenic to ordinary iron, we have made the tests recorded in Chart VI and Tables V and VI. Ordinary transformer sheet steel was melted into ingots, alone and with the addition of 5 per cent. of arsenic, then forged and turned into test bars. Examination of the magnetization curves shows a considerable improvement of the quality in the arsenic bar, with both materials inferior to the electrolytic.

Annealing at 675° has improved both bars, the arsenic bar still being superior in the lower ranges of magnetizing force, and being but very little inferior to the electrolytic sample. Further heating to 1000° resulted in a marked falling off in both bars, and the material free from arsenic gave the better results.

Summarizing, we have in this arsenic series some most interesting and unexpected results. In the first place, this element, with a temperature of sublimation of 450° C, alloys with iron under conditions where it has passed this temperature long before the fusion of the iron, in practically the proportions of the solid mixtures up to a content of arsenic of 4 per cent. Also we note

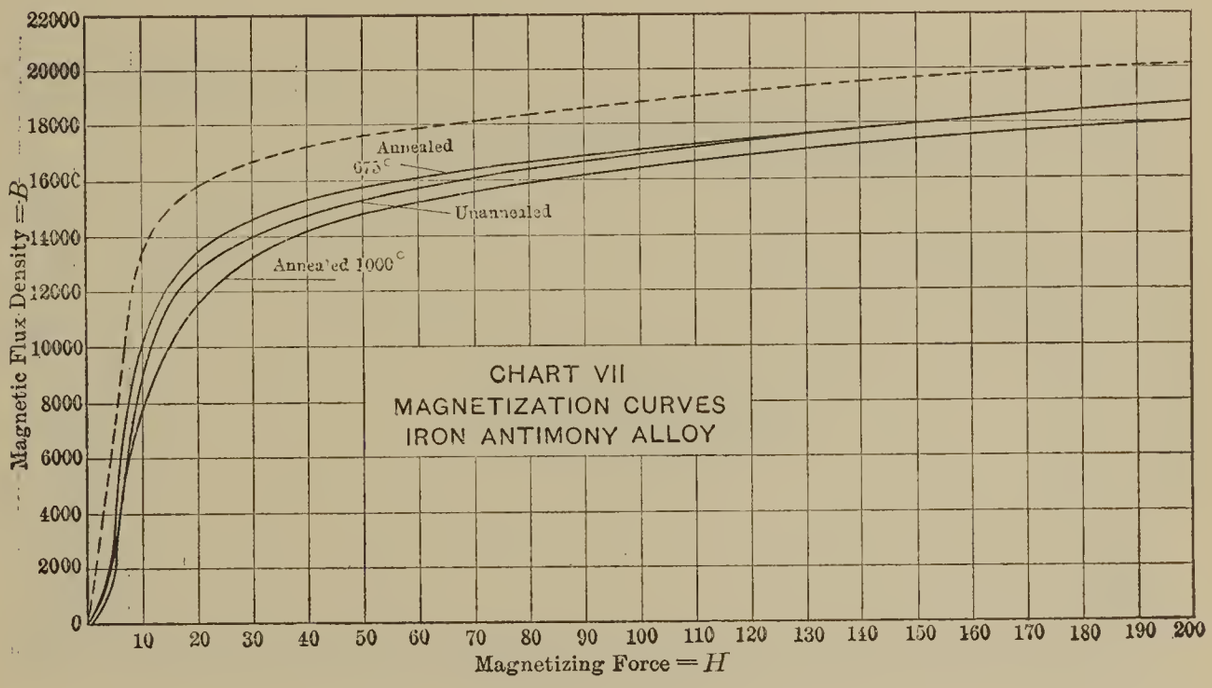


the more interesting feature that the presence of this large quantity of an element, which when present above 0.25 per cent. is most detrimental in its physical effects, imparts to the alloy magnetic qualities excelling those of the purest iron and on a par with the best material of which we have been able to obtain data.

Antimony.

Two sets of alloys with proposed antimony content of 1, 2, 4, 6 and 10 per cent. were made up and resulted in good ingots. In each case, however, but one of these with the lowest content of 1 per cent. was forgeable, and that only with difficulty. As in the case of the arsenic bars, magnetic tests were made of the

unannealed sample, and after successive annealings at 675° and 1000° C. A quenching test was not made. The magnetization curves are plotted on Chart VII and some of the data are collected in Tables V and VI. As compared with the electrolytic iron sample, the antimony alloy is of low grade. The same general effect of annealing is indicated as previously discussed; viz., an improvement upon heating to 675° and a deterioration after the second heating to 1000°. Also we note the same successive falling off in the coercive force, being 7.3, 5.0 and 4.0, respectively.



The antimony series, therefore, seems of little value, forming a difficulty workable product with no apparent value as a magnetic material.

Check analysis on the forged bar showed the presence of antimony of 1.15 per cent.

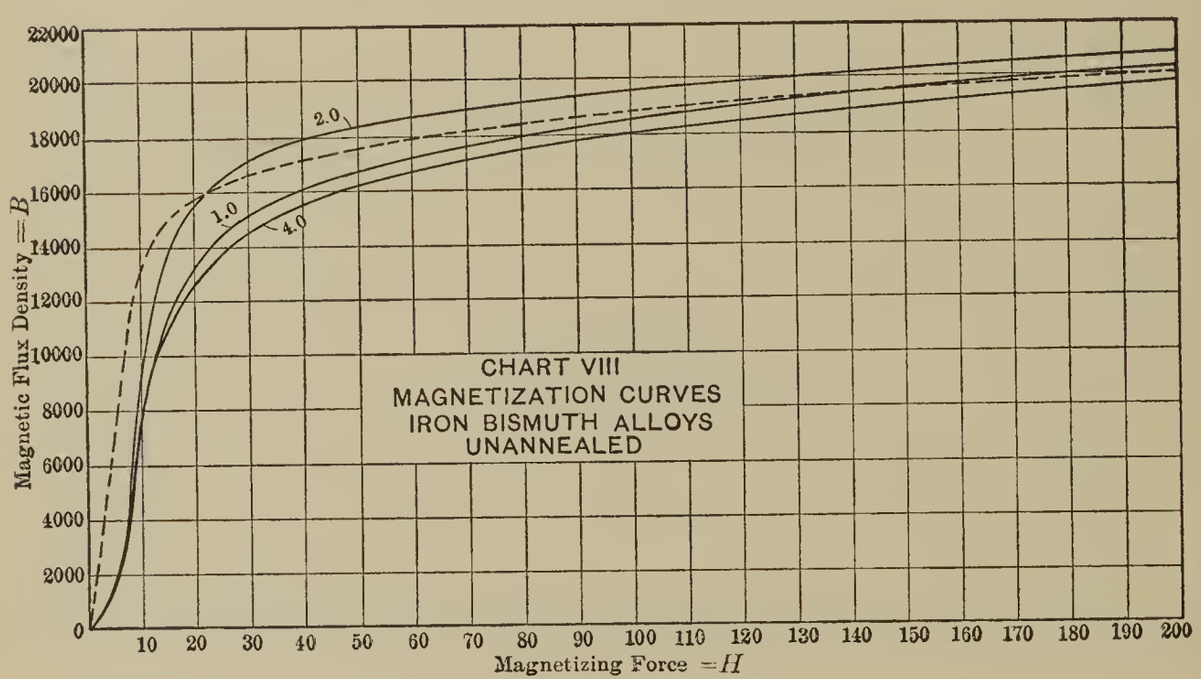
Bismuth.

A third element in this analogous group, the effect of which has been investigated, is bismuth. Alloys were prepared to have a bismuth content of 1, 2, 4, 6 and 10 per cent. The 2 per cent. ingot was lost in the melting, and the others were made into test bars and magnetization curves taken in the unannealed condition. However, all of these bars were lost in annealing and a second series was prepared of like composition, all of the

ingots being good. They were worked into bars with no special difficulty, either in forging or machining. Table VII gives the test numbers of these bars, together with the bismuth content.

TABLE VII.

Bar No.	Per cent. Bismuth As mixed	By analysis
172 G	1.0	.....
172 H	2.0	.....
172 J	4.0	.....
172 K	6.0	.....
172 L	10.0	.....

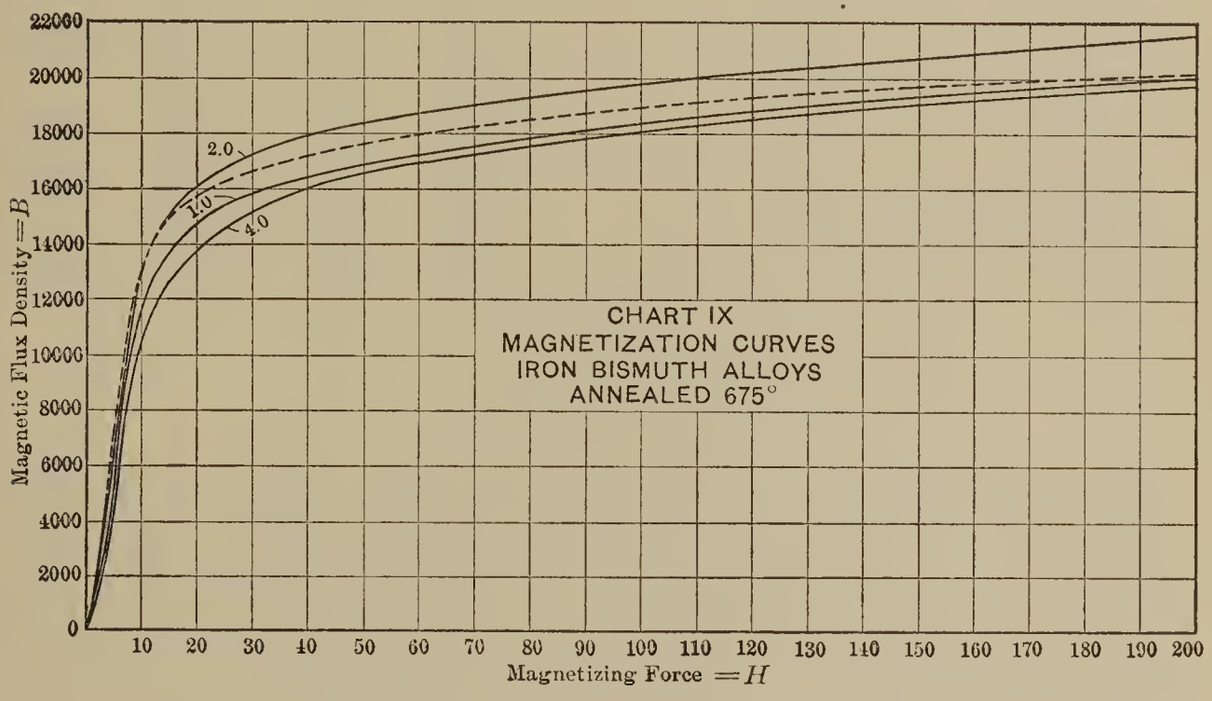


The magnetization curves under two conditions, as forged and as annealed at 675° C are plotted in Charts VIII and IX, and comparative data is tabulated in Tables V and VI. For all tests the curves for a bismuth content of 1.0, 4.0, 6.0 and 10.0 per cent. present no features of particular interest, the quality being well below the standard electrolytic iron sample. But for the bismuth content of 2 per cent., the curve, while below the standard for values of H of less than 22, at this point crosses the electrolytic curve and reaches values of density from four to five per cent. higher throughout the rest of the range.

Annealing at 675° C has not had much effect in these upper ranges of magnetizing force, but has been most beneficial in the lower portions, by making the quality equal to the standard for

these values of H, and lowering the crossing point to H = 10. The coercive force also has dropped from 7.0 as unannealed to 4.2 after heating. Further annealing at 1000° has caused a pronounced deterioration of the quality, and the 2.0 per cent. bismuth curve has taken a place in the midst of those of other percentages.

The general effect of the successive annealings is again the same as previously noted. The first heating to 675° C. has brought out the best magnetic qualities of the different alloys, with considerable improvement over the unannealed state; and further annealing to the higher temperature of 1000° C has



resulted in a deterioration. The coercive forces also have been markedly lowered with the first heating, but their values are relatively varying at the higher heating.

Summarizing, we have in this series the somewhat paradoxical condition of the addition of 2 per cent. of bismuth, the most diamagnetic element known, improving the already high quality of the pure iron. The density values reached with this material exceed those obtained with any of the several hundred different alloys which we have tested up to this time. Since analyses have not as yet been made to determine the amount, if any, of bismuth present in the alloys, it cannot be asserted that the intended content and actual content of bismuth are the same.

Definite conclusions as to the quantitative influence of bismuth must therefore be reserved until later.

TABLE VIII—COMPARATIVE RANK OF MATERIALS ON VALUE OF B, AT H = 20.

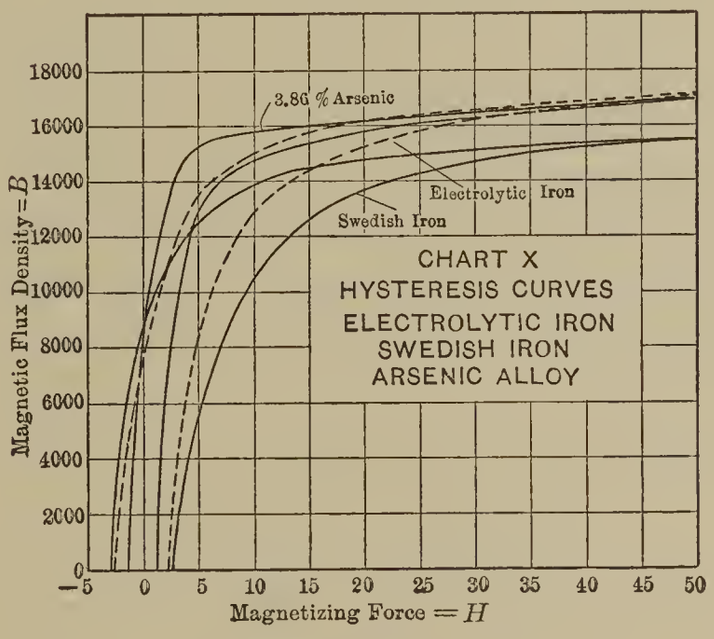
No.		Comp.	H = 10	H = 20	H = 50	H = 100
1	Kreusler's Annealed Rod of Dynamo Steel.....		15,680		17,100	18,280
2	Barrett-Hadfield's Alloy...	2¼ AL	15,300	17,000	18,000	
3	113 D	3.86 AS	15,050	16,300	17,550	18,650
4	172 H	2.0 Bi	13,250	16,100	18,350	19,750
5	113 H	3.56 AS	14,200	16,100	17,550	18,750
6	Sankey's Lohys Sheet.....		14,150	16,100	17,050	18,250
7	117 A	Elec.	10,000	15,950	17,700	18,850
8	113 F	4.14 AS	14,200	15,900	17,250	18,450
9	Hadfield's Magnet Steel...		12,150	15,900	17,350	18,200
10	Barrett Pure Iron.....		14,000	15,900	17,200	
11	113 B	1.81 AS	11,850	15,750	17,450	18,750
12	121 I	0.29 AS	13,200	15,550	17,250	18,550
13	Allen's Cast Steel.....		12,100	15,050	17,200	18,450
14	Barrett-Hadfield Alloy....	2½ Si	14,000	15,000	16,600	
15	High Grade Sheet.....		13,100	14,800	16,300	17,600
16	172 D	(Trans + 5 As)	9,550	14,750	16,750	18,000

COMPARISONS.

Magnetic testing is not on such a basis that data from various sources can be assumed as absolute, and on this account comparisons are apt to be misleading. While recognizing this fact we have nevertheless collected published data and compared them with our results in Table VIII. In this table is given the comparative ranking of several of our alloys, together with material tested by other investigators and the data for which was published because of the excellent magnetic quality. The material is ranked on the relative densities reached for a magnetizing force of H = 20, this value of H being taken because it is beyond the bend of the magnetization curve. Among the outside data we note the results of Barrett's tests (Inst. Elec. Engrs. Vol. 31) on pure iron (10) and on Hadfield's alloys of this iron with 2¼ per cent. of aluminum (2) and 2½ per cent. silicon (14), the last being the basis of the present silicon alloys so largely used in transformer construction. In this tabulation of sixteen tests there appear eight of our electrolytic iron, arsenic and bismuth series.

Table IX—Electrical Resistance.

		Microhms per cm.³	Relative
NSW	Swedish anode	11.6	0.96
117 A	Electro forged	12.1	1.00
Antimony.			
172 E	1.15%	20.2	1.67
Arsenic.			
121 I	0.292%	14.7	1.22
121 H	0.430%	16.8	1.39
113 A	0.915%	19.5	1.62
113 B	1.810%	25.5	2.11
113 D	3.862%	37.1	3.07
113 H	3.563%	34.0	2.82
172 C	Trans. sheet.	18.7	1.55
172 D	Trans. + 5% As.	30.2	2.51
Bismuth.			
172 G	1.0%	13.4	1.11
172 H	2.0%	14.5	1.20
172 J	4.0%	15.3	1.27
172 K	6.0%	13.0	1.08
172 L	10.0%	16.6	1.38



Hysteresis Tests.

On Chart X are plotted the hysteresis curves for bar 113 D, the 3.86 per cent. arsenic alloy; for the electrolytic iron sample, 117 A; and for the Swedish anode bar NSW. The half loop only is shown, with H (max.) = 50. Integration gives as the relative areas of the loops, 1, 1.7 and 2.1, respectively; and indicates the relative hysteresis losses per cycle of the materials in question.

Electrical Resistance.

In connection with these investigations, measurements of the electrical resistance of the magnetic test bars were made, and in Table IX are enumerated the results for the materials discussed in this paper. The specific resistances are given in microhms per cubic centimeter, and in the last column are tabulated the relative resistances with electrolytic sample 117 A as the basis of unity. Its resistance is but little different from the Swedish iron bar, being slightly higher, as a result perhaps of the heat treatments which the bars had undergone.

The addition of 1.15 per cent. of antimony has increased the resistance very markedly, from 12.1 to 20.2 microhms per cubic centimeter, or an increase of 67 per cent.

Additions of arsenic to the iron have also increased the resistance most markedly, the increase being a function of the percentage of added element. Bar 113 D, with 3.86 per cent. of arsenic, has a specific resistance of 37.1 microhms per cubic centimeter, or 3.07 times the resistance of the electrolytic samples. Likewise, the addition of the arsenic to commercial transformer sheet iron has raised its electrical resistance form 18.7 to 30.2 microhms per cubic centimeter, an increase of 62 per cent.

The bismuth alloys show but little increase of resistance, but definite deductions cannot be drawn from these figures, since the chemical analyses have not yet been completed to confirm our intended bismuth content.

Chemical Engineering Laboratories,
University of Wisconsin.

DISCUSSION.

Dr. W. R. Whitney: Mr. President, I recognize the truth of what Prof. Burgess has said, that it is difficult for any one to discuss a subject of this kind, where the methods of obtaining the data are difficult of manipulation. It is, unfortunately, true that it is hard to make comparative tests of the electric and magnetic properties of steel. I should be very glad to assist such work as Prof. Burgess is doing in any way possible, or to answer any

questions that I can answer on the methods of the treatment of steel, because I recognize that it is work that ought to be, and is likely to be, of very great value to the electrical industries of this country. Take the case of arsenic in steel for transformers—4 or 5 per cent. He has tested, as I understand it, the physical properties of that material, and found that it can be rolled and made into sheets. That is a very important matter, and possibly of great value to the electric industry of this country. All I want to say is that I for one appreciate, and have appreciated, the value of such work as Prof. Burgess is doing on iron.

Mr. Carl Hering: I also wish to express my appreciation of the great value of this work of Prof. Burgess. I would be pleased to know how he alloys the arsenic with the iron, in given proportions, because the volatilization point of arsenic is lower than the melting point of iron, so that much of the arsenic would be volatilized before it is gotten into solution with the iron. I ask this because there are special methods for doing this, one of which I understand is patented.

I notice also that he finds some impurities in the electrolytic iron. I would like to ask whether that could not be overcome by the use of porous cups. I have noticed that some of the particles which are suspended in the solution, travel with the current, as I described in a paper read before the Society,[1] and it seems to me that this explains how the carbon gets over to the electrolytic iron; if a porous cup were used, it would seem that it might prevent some of those impurities from reaching the electrolytic iron.

Concerning the comparison of magnetization curves, it seems to me that the difficulties might be overcome if some one material were agreed upon as a standard, and a whole lot of samples made of it and sent to the Bureau of Standards to have their curves determined; then let those who are interested in such comparative curves get a sample of that material and run that sample through their own apparatus. In that way it becomes possible to compare all curves with one standard, which has been accurately determined by the Bureau of Standards.

Mr. H. M. Hibbard: Mr. President, in regard to the remarks

[1] See "Visible Migration of Particles between Electrodes," Hering. Trans. Am. Electrochem. Society, Vol. X, p. 35.

of the last speaker about alloying iron and arsenic: It is very easy to alloy iron and sulphur. I believe sulphur in respect to its fusing point presents the same condition as arsenic does. Thirty years ago, when I was in the laboratory, I used to have to make sulphide of iron for the generation of sulphide of hydrogen. I took a crucible, filled it full of iron fragments, heated them red hot, added sulphur, and got sulphide of iron without any trouble. I dare say something like that could be done to make iron arsenic alloy, which then could be alloyed with the iron in any proportion that was desired.

Prof. C. F. Burgess: Mr. President, the remarks of Mr. Hibbard will, I think, answer Mr. Hering's question in reference to the possibility of alloying arsenic with iron. Alloys can be made, although the arsenic has a lower volatilizing point than the iron melting point. We perhaps made an error, although we did it knowingly, in calling this an alloy of iron and arsenic. It may be a mixture of iron with arsenide of iron under the particular conditions of working which we employed, that is, mixing the granulated electrolytic iron with arsenic in a closed magnesia crucible, and heating it somewhat rapidly in an electric furnace; percentages of arsenic subsequently found in the alloy were 4 per cent. Some of the arsenic, of course, volatilized out when the amounts put in were greater than 4 per cent.

As to the purity of the electrolytic material being increased by the use of porous cups, that undoubtedly could be secured. Some of the resultant impurity is doubtless due to entrainment, or physical mixture, of the electrolyte with the iron. The difficulty I would see in carrying out the suggestion of Mr. Hering, that the Bureau of Standards have one material which may be standardized by their methods and then furnished to other investigators, is that the different methods of testing require different sizes of samples, and it is difficult to get comparative results on account of the errors due to these varying sizes and shapes. In other words, the method of testing would have to be standardized.

Mr. E. S. Sperry: What was the amount of reduction in the reluctance below and above the anneal?

Prof. Burgess: In reference to the bismuth alloy, which has been designed as a 2 per cent. bismuth iron alloy—that is, a sup-

posed 2 per cent. bismuth content—shows a magnetic density of 20,000 lines per square centimeter, while the pure or electrolytic iron had a magnetic density of 19,000 per square centimeter. It is not a large percentage of increase, but it is some increase, and this is not so significant a point as is the apparent showing that the presence of a diamagnetic material, such as bismuth, will not harm the material.

A paper presented at the Meeting of the New York Section of the American Electrochemical Society, in New York City, April 3, 1909, and called up for Discussion at the Fifteenth General Meeting of the American Electrochemical Society, at Niagara Falls, Canada, May 6-8, 1909.

PROTECTION OF STEEL AGAINST CORROSION.—II.

By Maximilian Toch.

In a paper which I read at the fourteenth general meeting of the American Electrochemical Society, on October 30, 1908,[1] I outlined the present condition of the theory of corrosion, and gave detailed statements of my experiments concerning steel plates which had been passified with the use of chromic acid and its various salts, and in it I arrived at the conclusion that where steel was exposed to the elements, or unduly abraded, the passifying agent lost its inhibiting value, and the results, in all cases, were practically the same as those where a good paint was used without the intervention of a chrome salt. The difference between theory and practice in the case of building construction is apparent, if the handling of building steel is watched from the time it is loaded on the cars until it arrives at its destination, and no paint material is sufficiently strong to withstand either the sledge hammer blows which it receives during the course of its erection, or the rasping of the derrick chains which carry it from the dray to its ultimate position, so that no matter what is used, the general specification on building construction reads that the abraded portions of building steel shall be retouched before the field coat is applied. There are many instances where the foundation beams and the steel uprights of large structures have begun to deteriorate, not through the auto-corrosion which may take place in accordance with the theory of Messrs. Cushman and Walker, but through the forced corrosion due to a direct electric anode current in the presence of moisture in the ground or in the concrete surrounding the structure. There have been cases where a steel beam has corroded in a wall and the corrosion was of sufficient volume to crack the masonry which surrounded the beam, and caused the wall to bulge.

[1] Trans. Am. Electrochemical Society, **14**, 207, (1908).

I have outlined on several occasions that oxidation cannot take place, under any circumstances, in the absence of moisture, as the addition of water is a necessary element in the composition of ferric hydroxide, and the point which I wish to make clear is that it is necessary for this present generation to coat steel which is surrounded by either ordinary fireproofing masonry or bedded in concrete, with a material which shall have electric insulating qualities and moisture resisting qualities, rather than inhibitive qualities, for the inhibition is merely secondary, as the primary cause of the corrosive effect is water itself.

We hear much concerning the protective quality of concrete, but concrete as it is generally used contains rarely more than 15 per cent. of cement, and cement is the real protective agency in the prevention of corrosion. The concrete mixture is either composed of 1:2:4 or 1:3:5, the third number representing the aggregate, which is largely composed of broken stone. The physical characteristics of the material used precludes the possibility of a dense concrete, and the voids which are adjacent to the steel itself are largely the seat of rust producing agents. In order to make myself perfectly clear on this point, and assuming that these voids cannot be prevented, owing to the inability of any human being to work as perfectly and correctly as a machine does, there is all the more reason why a perfect coating of insulating material should be given the steel, rather than a perfect coating of such paint as shall itself be affected by moisture and be decomposed by moderate alkalies. It is not my purpose to speak either for or against any particular paint, and while I personally do not believe in lamp black, carbon black, or graphite paint as a *priming* coat because these paints have withstood the ravages of the elements as finishing paints, I am positive, from my past experience, and from pieces of steel which I have seen uncovered, that materials of this character, when mixed with linseed oil, form practically no protection for steel which is to be surrounded by alkaline and wet masonry of any kind. Some engineers have even gone so far as to require an inch coating of cement mortar, composed of one part of cement and one part of sand, before either the fireproofing or masonry is applied to building steel, but this practice—good as it is theoretically—fails very frequently when the priming coat is a saponifiable paint composed of

linseed oil, it being a medium which is easily attacked by water or the alkali of concrete.

If you take the case of a beam which is placed in a 12″ brick wall, and which is coated with a linseed oil paint, and then covered with an inch of cement mortar, a driving rain will go through such a wall and carry with it sufficient solvent salts to disintegrate the paint and leave a space between the steel and the concrete, and once corrosion starts in a place of this kind, we have only to refer to the excellent work done by Dr. Whitney (Journal American Society, Volume 4, April, 1903), which shows us beyond a question that corrosion can be progressive under such conditions, without the intervention of additional gas or moisture.

The remedy which I propose at this time has been thoroughly tried out for the past five years, and excavations have been made to determine whether such a material is lasting or not, and in every instance the result has shown that where an alkali-proof material has been used, which in itself is a guard against stray electric currents, there should be absolutely no fear for the permanence of our large and modern structures.

A paper presented at the Fifteenth General Meeting of the American Electrochemical Society, at Niagara Falls, Canada, May 8, 1909; President E. G. Acheson in the Chair.

SOME PHYSICAL PROPERTIES OF CRYSTALLINE SILICON.

By Clarence Irving Zimmerman.

It has been estimated by Clarke[1] that the element silicon constitutes 28 per cent. of the earth's crust. It exists in the form of its oxide, siO_2, and this oxide constitutes 60 per cent. of the earth's crust. Next to oxygen it is the most abundant element. The importance of knowing the various properties of silicon, which can now be obtained in a relatively pure state in any quantity desired, cannot be under-estimated. We know a great deal about the properties of such metals as aluminum, iron, copper zinc, tin, etc., and about such elements as sulphur, carbon, hydrogen, chlorine etc., but about the element that is more abundant than all others, with the exception of oxygen, we know very little.

I cannot offer an abundance of new information about silicon, but I wish to present some of the things that are known; and to thereby show that insufficient reliable information is at our disposal. No doubt considerable recently obtained data could be added to, or substituted for what is given below, and if any can be added or substituted, I hope this paper will assist in bringing it to light.

Not only might such information be of great value in finding valuable applications for the element, but it would probably lead to the correlation of many properties which the various elements and many compounds have in common.

Below is given a brief summary of some of the physical properties of silicon.

1. *Atomic Weight*—28.4.

2. *Specific Gravity*—2.35

Silicon is lighter than aluminum, the latter being 2.56—2.68.

[1] F. W. Clarke, "The Data of Geochemistry," U. S. G. S. Bull. 330, 31 (1908).

3. Molecular State of Aggregation—

Silicon is definitely known to exist in but two well-defined states (1), the amorphous, or finely divided non-crystalline state, and (2) the isometric crystalline state.

Moissan and others assert that the "graphitoidal" state of silicon does not exist. It has been shown to be the same as the isometric crystalline silicon.[2]

According to its method of preparation and according to the rate at which it passes through the change of state from liquid to solid, the crystal habit and the sizes of the crystals themselves will vary, but the crystalline system remains isometric.[3] The element crystallizes in needle-shaped forms, in flat plates and in skeletal crystals, all of which may present the appearance of rhombohedral and hexagonal forms. When crystalline silicon is made by the reduction of silicon dioxide by sodium in the presence of zinc, the needle-like crystals formed are isometric octahedral forms. When silicon is made by the reduction of silicon dioxide by aluminum, thin plates are frequently formed, which appear to belong to the hexagonal system, but which have been shown to be isometric. When silicon is tapped from the electric furnace it solidifies to a massive crystalline material, with variable sized crystals. A considerable quantity of gas is frequently found between the crystals or in pockets like "blow-holes." If the solidification takes place very slowly, a very homogeneous, but coarsely crystalline, material may be obtained which contains no cracks or blow-holes. Under some conditions of very slow cooling the degree of crystallization is so extreme that the material can be picked to pieces with the fingers, the separations taking place along cleavage planes.

When solidifying, silicon appears to expand. This is partly, but is not entirely, due to the giving off of gases.

Some masses appear to be under a severe molecular strain. Conchoidal fractures are readily obtained, but when the crystals are small the fracture in cast silicon usually occurs along crystal faces or less readily on cleavage planes. Cleavage in massive specimens becomes evident when a plane surface is ground by means of an abrasive. The various crystals in the mass show

[2] H. Moissan, "Traite de Chimie Minerale," Ed 1905, Vol II, p. 596.
[3] Ibid. See also Roscoe & Schorlemmer, "Treatise on Chemistry," Vol. I, Ed. 1905, p. 875.

their different orientation by the reflecting surfaces from the cleavage planes. Mr. A. B. Albro showed a number of photographs of this in a paper presented before this society in 1907.[4]

An extremely thin lamellar variety of crystalline silicon has been described by Moissan.[5] It is so thin that it is transparent. It is slightly yellowish in color. It is more resistant chemically than the usual crystalline forms. This form was obtained by the separation of silicon from molten silver, and is stated to be somewhat similar to the material originally thought to be graphitoidal. I have observed considerable quantities of material, which appears to be the same as that which Moissan described. This was found around nodular masses of silicon, slowly cooled in the bottom of an electric furnace, but its identity with crystalline silicon was not at the time established. The flakes are usually so thin as to present interference colors.

4. Tenacity—

Silicon is very brittle and is especially so in the cast form. The rate of cooling through the solidifying point, and probably the rate of cooling below the point of solidification affects the brittleness to a very marked extent. Cast silicon often, if not always, becomes more brittle by repeatedly heating it to a red heat and quickly cooling it in water. Aluminum, iron, manganese, and probably many other metals will bind the crystals in cast silicon together and toughen the mass somewhat, but for many purposes the presence of foreign elements or alloys is undesirable. The silicon itself is extremely resistant chemically and so its properties will necessarily be somewhat different when any foreign material is introduced which is less resistant than silicon.

No results on the proper rate of cooling silicon castings in order to give the strongest and toughest casting have been published.

5. Expansion with Temperature—

No recent data on pure silicon are at present available. In 1864, Fizeau[6] made some measurements upon crystalline silicon and found that the average co-efficient of expansion from

[4] A. B. Albro, "The Micro-Structure of Silicon and Silicon Alloys," Trans. A. E. Soc. **11**, (1907).

[5] H. Moissan, "Traite de Chimie Minerale," Ed. 1905, Vol. II, p. 597.

[6] Fizeau Ann. Chem. Phys., [4] **2**, 143 (1864).

0-100° C. was 0.0000078. This would appear to be less than glass or platinum. The expansion co-efficient varies with the temperature. It should be correlated with the electrical resistance curves shown in a later part of this article.

6. Tensile Strength—

The highly crystalline state and the brittleness frequently prevent its use where small and delicate plates or rods are required, but in larger masses these objections partly disappear. No figures on the tensile strength of large masses are available. When rods are cut from blocks of homogeneous silicon the strength is apparently much greater than the strength of cast specimens. Rods cut from these homogeneous specimens might therefore be applicable where cast rods are not suitable.

7. Hardness—

On the scale of hardness used in determining the hardness of minerals, silicon would be about six. It is like steel in hardness.

8. Porosity—

As was stated above, silicon is frequently porous due to the gases which were liberated from the liquid mass when it changed its state. The openings sometimes do not appear to be present when they are really there. The openings may be between crystal faces. It is not impossible, however, to make solid castings or blocks.

9. Melting Point—

Mendenhall and Ingersoll[7] found the melting point to be 1434° C. based upon the assumption that platinum has a melting point of 1745° C. With an assumed value of 1789° C. for platinum they have given the figure of 1452° C. for silicon. I have obtained a melting point of 1430° C. in an electric furnace, the measurement having been made by a platinum-rhodium thermocouple. The couple was calibrated by the Deutsche Reichsanstahlt, but I do not know what value was assumed for the melting point of platinum on that calibration scale. Mr. F. J. Tone has also given a melting point of 1430° C. for silicon[8]

[7] Mendenhall & Ingersoll, Phys. Rev., **25**, 1 (July, 1907).
[8] Tone. Trans. A. E. Soc., **7** (1905).

10. Vapor Tension—

The vapor tension of silicon is practically zero up to the temperature of its melting point. In the presence of air silicon becomes superficially oxidized, and this oxidized surface protects the silicon from further oxidation at high temperatures. Above its melting point oxidation readily takes place and a loss of silicon will occur by oxidation. In the vacuum furnace silicon may be easily volatilized.[9] It is quite probable that above 1800° C. the vapor tension from the surface of liquid silicon is considerable, or many of the reactions known to occur in the silicon and carborundum furnaces could not be explained. Dr. H. N. Potter assumes a contrary view in his "Monox" papers.[10] In the presence of free carbon at high temperatures silicon combines with carbon. In silicon carbide the silicon has a very much lower vapor tension that when the element is free. At the temperature of decomposition of silicon carbide, and in a carborundum furnace, silicon is a vapor. The temperature of the decomposition of the carbide will vary with the amount of silicon dioxide vapor present. The boiling point of silicon at 760 mm. pressure is probably over 2000° C., and may be even higher than 2500° C.

11. Specific Heat—

I am not aware of any recent determinations on the specific heat of silicon over a wide range of temperatures. Silicon, like carbon, changes its specific heat widely. Above 200° it is supposed to be constant. Weber[11] made some measurements a long time ago.

Temperatures.	Specific Heat.
—40	0.136
—57	0.1833
128	0.196
184	0.201
232	0.203

[9] Arsem., Trans. A. E. Soc., **7** (1905).
[10] H. N. Potter, Trans. A. E. Soc., **12**, 194 (1907).
[11] Weber, Phil. Mag., [4] **49**, 161, 276.

12. Latent Heat of Fusion—

No data available. When making castings of silicon the material passes very quickly through the change from the liquid to the solid state. The latent heat of fusion seems to be quite low, or else silicon is an excellent heat conductor at its melting point.

13. Heat of Combustion—

Considerable work has been done recently upon the heat liberated when the element oxidizes. W. G. Mixter[12] obtained a figure of 191,000 calories per 28.4 grams of silicon burned to silicon dioxide. Dr. H. N. Potter[13] obtained a figure of 215,000 calories per 28.4 grams of silicon burned to silicon dioxide. Without other confirmations I think it would be best to consider the value unsettled and that 191,000 calories per 28.4 grams is the more conservative figure. The rate of energy liberation when silicon combines with the oxygen of various metallic oxides in silico-thermic reactions seems to indicate that the higher figure may be doubtful.

14. Thermal Conductivity—

The thermal conductivity seems to be quite high. This element has a low electrical conductivity and a high thermal conductivity. It does not seem to act the same as ordinary metals in this respect, but it is not the only exception in this anomaly.

15. Optical Properties—

Silicon has a dark silvery metallic lustre having a bluish tint, something like that of a freshly cut lead surface. The surface does not tarnish or corrode. A polished surface will thus remain almost indefinitely without losing its lustre. The reflection of light from a polished surface is not nearly so perfect as from a silver surface, but for some optical and for ornamental purposes it might be valuable. When very thin, it is translucent.

Silicon has a high refractive index. In this respect it is similar to its carbide.

Very finely powdered silicon is brown in color, resembling the amorphous variety in this respect.

Its optical properties are being investigated at present.[14]

[12] Mixter, Am. Jour. Sci., 24 (Aug., 1907).
[13] H. N. Potter, Trans. A. E. Soc., 11, 263 (1907).
[14] Littleton and others, Physics Laboratories, University of Wisconsin.

16. Spectrum—

The flames which come from a silicon or a carborundum furnace are of a greenish yellow color. The silicon flame color is usually masked by the ever present sodium flame. With a small pocket spectroscope there are eight or nine prominent lines observed and many very faint ones.

Silicon Furnace Flame-Colors—

Deep Red	2 lines
Orange	1 "
Yellow (Na)	1 "
Green	2 "
Blue and Violet	4 "

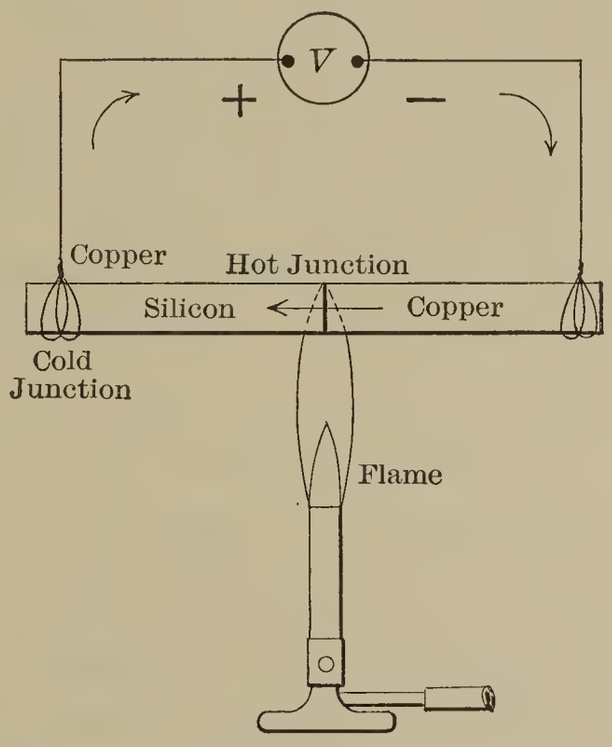


FIG. 1

Direction of thermo-current in most of the writer's samples.

For accurate work and data on the silicon spectrum, see books on spectroscopy.

17. Magnetic Properties—

St. Meyer[15] published some data on the magnetic behavior of silicon. For all practical purposes it is non-magnetic. Silicon-iron alloys will decrease in magnetic susceptibility until the silicon content increases to 30 per cent. Above 30 per cent. of silicon, the silicon-iron alloys are practically non-magnetic.

[15] St. Meyer, Weid. Ann., **69**, 236 (1899).

18. Electrical Properties—

The electrical properties and constants of silicon are exceptionally interesting because they are quite different from metallic conductors. Some of these will be discussed below.

18A. Thermo-electric Properties—

Heath[16] found that the junction of silicon and metals exhibits high thermo-electromotive forces when heated.

The magnitude and the direction of the electromotive force generated will vary greatly in different specimens. Sometimes the current will flow in one direction across the hot junction and sometimes in the opposite direction. A single specimen may have positive and negative spots. This peculiar ability of a given substance to exhibit high thermo-electric forces in different directions at the contact with a metal or other conductor is not new, nor is it characteristic of silicon alone. It is quite a common phenomenon among mineral substances, and was investigated to some extent twenty-five years ago.[17] Miss Francis G. Wick[18] and Dr. L. W. Austin[19] have published some results on the thermo-electromotive forces of silicon-metal contacts. They have stated that the usual direction of current flow is from silicon to copper through the hot junction. My own observations are just the reverse. The usual direction is from the copper to the silicon across the hot junction in a copper-silicon couple. I have tested this out on forty or fifty different specimens of silicon which covered a wide range of physically and chemically different samples. I have also tried a number of alloys of silicon against a metal and have found that in nearly all of the cases the silicon was the positive side of the hot junction as is shown in Fig. 1. The few specimens which did not follow my above described usual thermo-electric direction at ordinary temperatures, reversed their effect when the temperature of the silicon itself was raised considerably above the temperature at which the first observation was made. There was no reversal of direction in what I have called my normal specimens even when they were raised to a

[19] Austin, Bull. Nat. Bur. Standards, Aug., 1908.

[17] Schrauf & E. S. Dana, Am. Jour. Sci., 8, 255 (1874).
Rose, Pogg, Ann. **142**, 1 (1871).
Friedal, Ann. Chem. Phys., **17**, 79 (1869).
Friedal, C. R., **78**, 508 (1874).

[18] F. G. Wick, Phys. Rev., **25**, 382.

[19] Austin, Bull. Nat. Bur. Standards, Aug. 1908.

very much higher temperature than that which reversed the abnormal specimens. Further work on this line is in progress.

18 B. Rectifying Properties—

The characteristic unilateral or asymmetric conductivity which is observed at the contact surface between almost any two heterogenious conductors is quite marked at the contact surfaces between silicon and metals. The current will pass across a silicon-metal junction much more readily in one direction than in the other. If the area of contact between silicon and a metal be varied the degree of unilateral conductivity for a given current flow will also vary. Hence, if an electric circuit contains a piece of silicon held between two metal contact pieces, and if the areas of contact on each side of the silicon are different, that circuit will be a unilateral conductor. If an alternating current be then passed through this circuit which possesses asymmetric or unilateral conductivity, there will be a tendency to stop one-half wave and to pass the other half wave. G. W. Pickard[20] was probably the first person to note that this effect could be utilized for wireless telegraph waves when silicon was one of the rectifying elements.

Extensive use of the silicon rectifier has been made in wireless telegraphy.[21] By a proper disposition of silicon rectifiers and of electrical condensers the energy of the short oscillatory trains of waves caught by an aerial can be stored in the condensers and subsequently discharged through a telephone receiver or through a galvanometer. Without rectification and without any means for storing the energy caught by the aerial the telephone receiver will not detect the waves. The condenser may be the aerial itself, or the telephone receiver coil. I have constructed some exceedingly sensitive wireless receiving circuits based upon the use of two or more of such crystal rectifiers with electrical condensers. Ordinarily only one such rectifier is used in commercial receiving circuits, and in such cases only a part of the energy of the oscillatory waves can be detected. The direction of the first half-wave of a strongly damped oscillatory train makes a great difference in the sensitiveness of a receiver containing only one silicon detector or rectifier. In this case

[20] G. W. Pickard, U. S. Patents, 836,531; 877,451; 888,191.
[21] G. W. Pickard, Elect. Rev. & West. Elect., Feb. 20, 1909.

much of the energy and also the highest electromotive force of the damped waves comes in the first pulse.

There is no thermo-electric action in the silicon detector.

It is an interesting phenomenon, still to be explained, that the thermo-electric and rectifying actions of silicon-metal contacts and other similar "crystal rectifiers" are usually such that the current flows through the rectifying contact in opposite directions in the two different cases. No doubt there is a simple explanation for this relation.

Just as there are numerous substances which, when placed in contact will produce high thermo-electric forces when the junction between the two of them is heated, so there is a long list of substances which show a marked rectifying action like that which silicon exhibits. Carbon and tellurium show these thermo-electric and rectifying effects to a marked degree when in contact with other conducting substances. The list of conducting mineral substances which show this same effect is too long to be given here. Almost all of them show this to a more or less marked extent.[22]

18 C. Hall Effect—

When a current of electricity flows across a conducting silicon plate, which lies perpendicular to the direction of a strong magnetic field, the current in the plate will take a different course than when the strong magnetic field is not present. The path of the current tends to be rotated more and more as the magnetic field increases. In silicon this effect is quite marked.[23] It varies greatly with different samples of silicon and is roughly related in magnitude to the thermo-electric forces. Dr. Smith[24] has investigated the Hall effect quite extensively in silicon and other substances. In silicon he finds the Hall effect is a reversible affair, like the thermo-electric and rectifying properties and that they are closely related.

18 D. Electrical Resistance—

The electrical resistance of silicon also shows some exceptionally varied and interesting results.

[22] For interesting and valuable data, see Pierce, Phys. Rev., March, 1909; also Pickard's Article, El. Rev., Feb. 20, 1909.

[23] F. G. Wick, Phys. Rev., Aug., 1908.

[24] Dr. Smith, *loc. cit.*, Results as yet unpublished. Phys. Labs., University of Wisconsin.

Two years ago Dr. C. P. Steinmetz[25] presented before this society in a lecture on "Conduction," some results on the relations between temperature and electrical resistance. He classified electrical conductors in a general way and stated that the resistance of certain specimens of cast silicon seemed to give an intermediate link between pyro-electrolytic and metallic conduction. Miss. F. G. Wick[26] investigated the electrical resistance of some

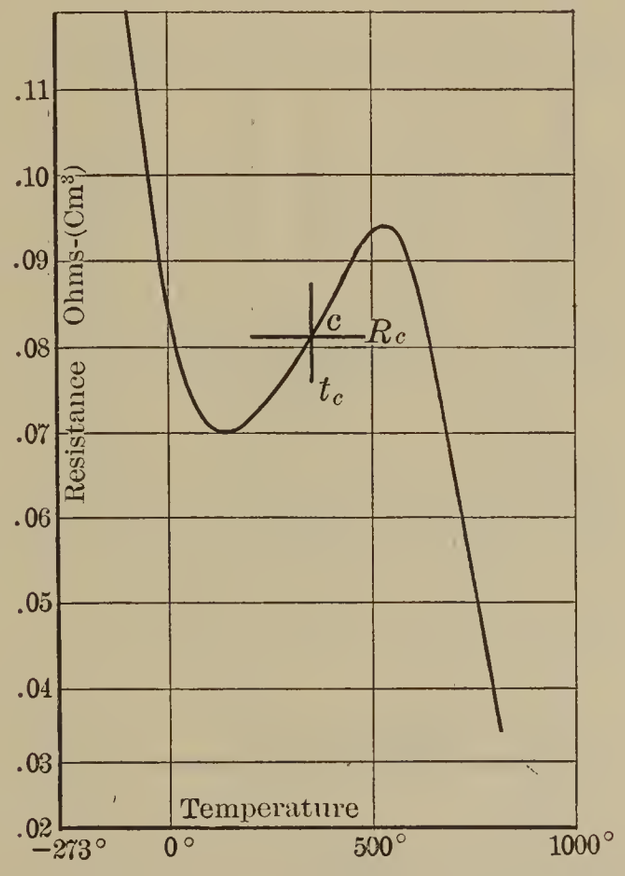


FIG. 2

Resistance—Temperature Curve. Silicon Rod No. 1

$$\text{Res} = R_c + m\,[K^2\,(t - t_c) - t - t_c)^3]$$

$$\text{or Res} = R_c\,[1 + n\,K^2\,(t - t_c) - n\,(t - t_c)^3]$$

rods of silicon similar to those which Dr. Steinmetz discussed. The results showed that cast silicon varied widely in its resistance characteristics in different specimens. Some specimens showed a negative temperature co-efficient through the range of temperatures which they studied, whereas other specimens showed a temperature co-efficient which was at first positive and afterward negative, and still others showed a change from nega-

[25] Dr. Steinmetz, "Conduction," Trans. A. E. S., **11**, 105-113 (1907).

[26] F. G. Wick, Phys. Rev., July, 1908, **27**, 11, "The electrical resistance of silicon at various temperatures."

tive to positive and then back to negative characteristics. Cast silicon rods were used in their measurements.

In Figs. 2 and 3 are shown curves plotted from experimental data which I have obtained from two specimens of silicon rods which were cut from homogeneous masses of slowly cooled, relatively pure and coarsely crystallized material. The temperature

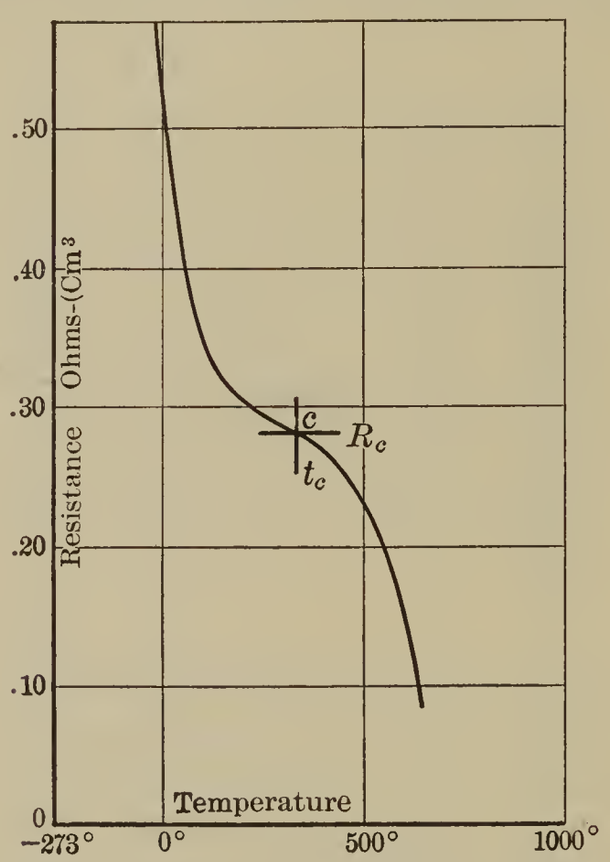


FIG. 3

Resistance—Temperature Curve. Silicon Rod No. 2

$$\text{Res} = R_c + m\,[K^2\,(t - t_c) - (t - t_c)^3]$$

$$\text{or Res} = R_c\,[1 + n\,K^2\,(t - t_c) - n\,(t - t_c)^3]$$

range covered was 190° C. to 800° C. The composition of these rods I give below:

Rod No. 1.		Rod No. 2.	
Impurities Present.		Impurities Present.	
Fe	— 0.32%	Fe	—
Al	— 0.14%	Al	—
C.	— trace	C.	—
Ca,Mg,Mn	— trace	Ca,Mg,Mn	—

In Figs. 2 and 3 there exists a cubic relation between the co-ordinates of the curves. In order to show this cubic relation more

plainly I have drawn two curves in Fig. 4 from the equation of a cubic curve having the formula

$$y = m(K^2x - x^3)$$

In curve 1, $m = 0.2$ and $K^2 = 30$.
In curve 2. $m = 0.02$ and $K^2 = -30$.

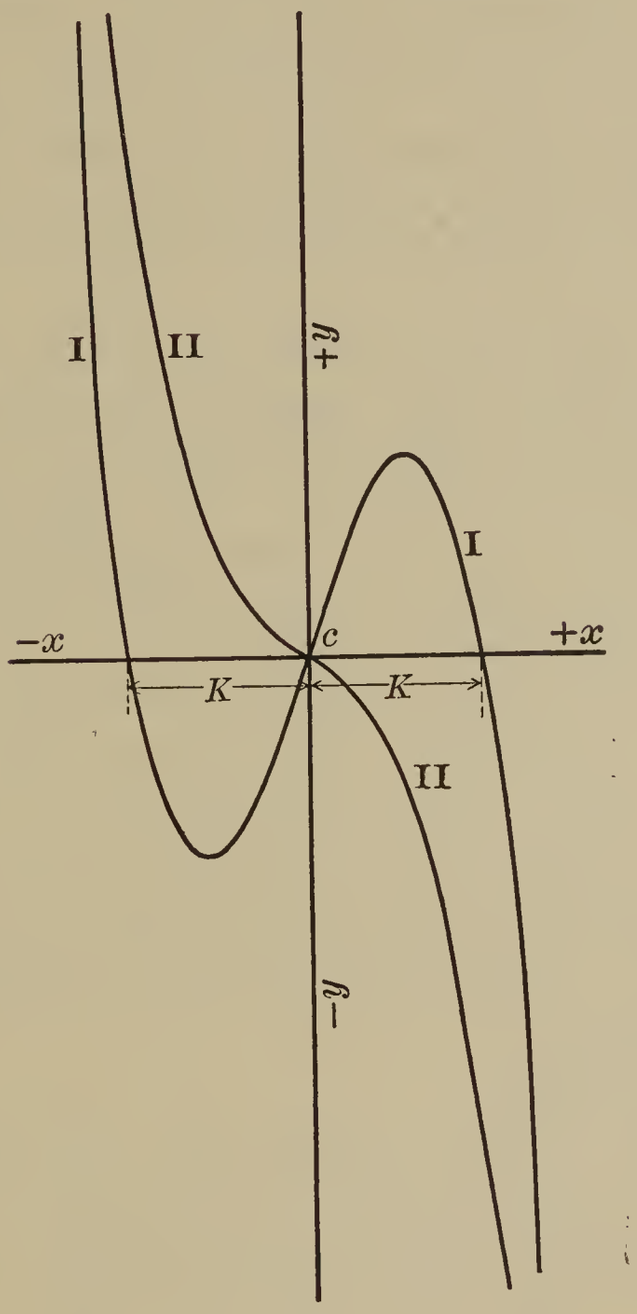


FIG. 4

Cubic Curves.

$Y = m(K^2 \times - \times^3)$

Curve 1 $\begin{cases} m = 0.2 \\ K^2 = 30 \end{cases}$ Curve 2 $\begin{cases} m = 0.02 \\ K^2 = -3 \end{cases}$

In curve 1 of Fig. 4, the factor K is equal to the horizontal distance between the centre of the cubic curve and the points at which the curve cuts the axis.

In curve 2 of Fig. 4, K is an imaginary quantity, as it is the square root of the negative quantity — 30.

The close resemblance between the experimentally determined curves shown in Figs. 2 and 3 and those drawn from the formula $y = m(K^2x - x^3)$ and shown in Fig. 4 is striking. Were this relation exact, the general formula for the resistance of silicon rod No. 1 would be exactly the same as the formula for the resistance of silicon rod No. 2. For rod No. 1, the factor K^2 is a positive quantity and for rod No. 2 the factor K^2 is a negative quantity. The factor m would be the same for both rods if the scales for the co-ordinates of temperatures and resistance were the same.

Since the origin of co-ordinates in the curves shown in Figs. 2 and 3 is not at the center of either of the curves, the formula for the resistance-temperature relations of the silicon rods is not quite so simple as the formula for the curves shown in Fig. 4. The constants which must be applied to the theoretical formula in order to make it apply to the experimentally determined curves have very interesting physical significances. At the present writing I do not wish to draw any general conclusions, as I wish to continue these investigations with different silicon rods.

As a theoretical formula for the resistance of the silicon rods assuming the curves to be true cubic curves, and referring the curve to the co-ordinates used for plotting the curve we get:

$Res = m(K^2t - t^3)$—Referred to centres of curves.

$Res = Rc + m[K^2(t - tc) - (t - tc)^3]$ Referred to the co-ordinates as plotted.

This may be written

$$Res = Rc[1 + nK^2 (t - tc) - n(t - tc)^3]$$

or again, by collecting constants and variables,

$$Res = a + bt + ct^2 + dt^3.$$

The cause of the marked differences in the specific resistance of the two rods is not yet definitely known. It may be due to the difference in the chemical composition alone, but it is probably due largely to a difference in the physical condition of the molecular aggregates in the two samples.

Further investigations are in progress.

I have attempted in this paper to show some of the unknown properties which are still to be investigated with the element silicon. There are so many interesting and valuable scientific phenomena which can be observed in studying the properties of silicon and which relate not only to the element itself, but to many other substances, that I think the Carnegie Institution or some other similar organizations should see to it that the investigation of the properties of the element which is second only to oxygen in abundance in nature, progresses more rapidly.

I wish to express my obligations to the Physics Department of the University of Wisconsin for placing at my disposal apparatus and facilities for making many of these observations and determinations. I also desire to thank Mr. Frank J. Tone and the Carborundum Company, of Niagara Falls, for considerable assistance rendered in the analysis of a number of samples of silicon.

Madison, Wisconsin,
April, 1909.

A paper presented at the Fifteenth General Meeting of the American Electrochemical Society, at Niagara Falls, Canada, May 8, 1909; President E. G. Acheson in the Chair.

RELATIVE EFFICIENCY OF THE ARC AND RESISTANCE FURNACE FOR THE MANUFACTURE OF CALCIUM CARBIDE.

By S. A. Tucker, W. A. Alexander and H. K. Hudson.

The object of this investigation was to determine the relative efficiency of the two types of electric furnace in the manufacture of calcium carbide.

In the arc furnace the temperature in or near the arc itself must be far in excess of that necessary to form calcium carbide. The temperature of the arc may be taken as about 3700° C. For the formation and actual fusion of calcium carbide Lampen[1] found the temperature to be 1800° C.

It is therefore probable that there is a very considerable decomposition of the carbide formed in the arc furnace, with a resulting low yield and consequent contamination of the product with graphite derived from dissociation of the carbide molecule.

In the resistance furnace the temperature can be regulated and held at a point much below that of the arc, and should produce calcium carbide in a more efficient manner than the arc furnace.

The following results show that this view is correct for the scale on which the experiments were conducted, and also give information on the best proportion of the charge, together with the proper manner of heating.

Arc Furnace Method.

The furnace used in the experiments was a slightly modified form of a type of vertical furnace described by one of us.[2]

[1] Journal Am. Chem. Soc., 28, 846.

[2] S. A. Tucker. Electro-chemical and Metallurgical Industry, 4, 263.

The dimensions of the graphite crucible as shown in Fig. 1 are as follows:

Exterior	diameter	at top	127 mm.
Interior	"	" "	108 mm.
Exterior	"	" bottom	127 mm.
Interior	"	" "	70 mm.
Exterior	height		146 mm.
Interior	"		127 mm.

The electrode used was of graphite, about 250 mm. long, and 25 mm. in diameter.

The run was conducted as follows. A charge was made up of 250-300 gms. of powdered coke and freshly powdered lime,

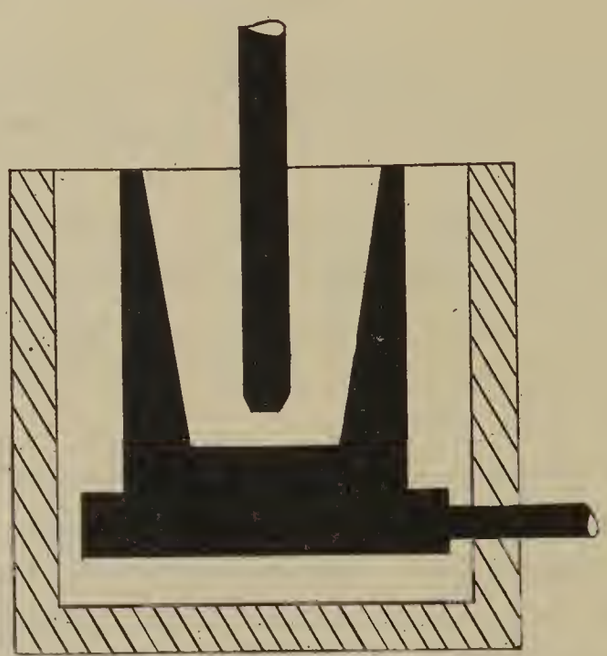


FIG. 1.

thoroughly mixed. The proportions of these constituents of the charge varied for the different runs and will be found in the tables. The arc was first struck and the charge added a little at a time and the electrode gradually raised as the run proceeded. The time of run was about eight minutes. After cooling, the carbide was weighed and sample taken for testing and analysis.

Resistance Method.

In the resistance method the current passing through the charge itself furnishes the necessary heat for the formation of the carbide.

A furnace of the following dimensions was set up as shown in elevation and plan in Fig. 2:

Exterior	length	455 mm.
"	width	355 mm.
"	height	145 mm.
Interior	length	227 mm.
"	width	102 mm.
"	height	102 mm.

The furnace was made of common fire-brick with the bottom made of magnesia brick. Distance between graphite electrodes was 140 mm. The electrodes were arranged so that during the

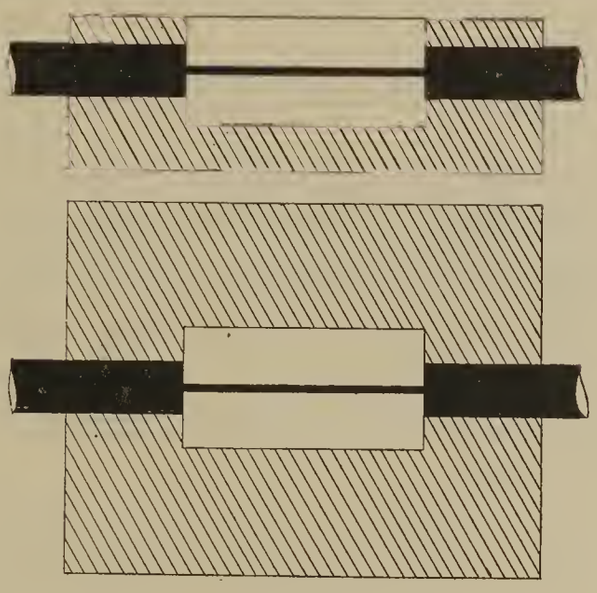


FIG. 2.

run the distance between them could be varied by sliding their supports in or out. The electrodes were 50 mm. in diameter. At start of run the circuit between the electrodes was made by a carbon rod 10 mm. in diameter. This was fastened into the electrodes by boring a hole in each electrode about 30 mm. deep. This rod was 38 mm. from the bottom of the furnace.

A charge of 2½ kilos of the same materials as used in the arc method was made up and placed in the furnace. This completely filled the furnace. At start of run a current of 100 amperes was used to heat up the charge. The e. m. f. was about 15 volts. After a short time the carbon rod burned away and the heated charge conducted the current between the electrodes.

It was always necessary to lessen the distance between the

electrodes a short time after the start of run. This was probably due to the fact that as the rod burned out the resistance of charge was too great for the voltage to force much current through it. Pushing the electrodes together cut down the resistance and thus allowed more current to flow. The current was gradually raised to about 300-500 amperes at end of run. The voltage went up to about 30 volts. Readings were taken every minute of volts and amperes. The time of a run was about twenty-five minutes. At the bottom of furnace a solid mass of carbide was formed that extended from one electrode to the other. When cool it was easily separated from the electrodes, weighed, and a sample taken for testing and analysis.

Testing and Analysis.

After each run a piece of carbide was placed in water and the gas evolved was lighted. Ease with which gas burned was noted. This together with the size of crystals gave a rough idea of the quality of the product. It was found that the larger the crystals the better was the quality of the carbide. To get a quantitative result the loss-by-weight method of analysis was used. The method follows:

The apparatus used consisted of a 400 c. c. Erlenmeyer flask fitted with a two-hole rubber stopper. Connected to the flask were a calcium chloride tube and a 125 c.c. dropping funnel. The calcium chloride tube was filled with fairly finely broken $CaCl_2$ and the dropping funnel with a concentrated solution of NaCl. This apparatus was put together and weighed on a large Becker analytical balance. The sample to be analyzed was broken into pieces about 15 mm. in diameter. Three to 4 gms. were put in the Erlenmeyer flask and the apparatus again weighed. This gave the weight of the sample taken. The NaCl solution in the dropping funnel was then allowed to run in very slowly—about 10 drops per minute. Considerable heat was evolved, but no water was lost as it was all absorbed by the $CaCl_2$ through which it passed. After the carbide was completely decomposed and the apparatus had cooled down to room temperature, air was drawn into the apparatus to replace the acetylene by air. It was then weighed again, and this gave the weight of the acety-

lene that was evolved. The percentage of acetylene and carbide are then calculated. NaCl solution was used to decompose the carbide because acetylene is insoluble in NaCl solution.

Experimental.

In Table I is given the data obtained in the arc furnace, in Table II that in the resistance furnace.

Table I.

No.	Charge		Weight in Grams	Time Minutes	Average Volts	Average Amperes	Watt Hours	Yield in Grams	Product	Actual Carbide Grams	Watt hours necessary to make 100 Grams CaC_2
	Coke	Lime									
1	40%	60%	276	8	80	149	1162	141	38.4%	54.1	2140
2	40%	60%	276	9	69	207	1758	141	38.8%	54.7	3200
3	45%	55%	300	5	67	186	863	140	52.7%	73.8	1170
4	50%	50%	300	8	70	188	1380	134	65.9%	89.3	1550
5	60%	40%	300	9	64	205	1583	100	73.4%	73.4	2160
6	55%	45%	250	8	61	200	1341	65	73.6%	47.8	2820
7	55%	45%	250	8	64	205	1576	60	76%	45.6	3430

Table II.

No.	Charge		Weight in Grams	Time Minutes	Average Volts	Average Amperes	Watt Hours	Yield in Grams	Product	Actual Carbide Grams	Watt hours necessary to make 100 Grams Ca C
	Coke	Lime									
1	40%	60%	2200	27	34	209	3147	1022	49.8%	509	618
2	40%	60%	2150	22	19	218	1487	402	50.6%	203.4	731
3	45%	55%	2000	21	30.5	243	2474	517	70.6%	365	678
4	50%	50%	2000	19	30	280	2683	520	84.9%	441.5	608
5	55%	45%	2000	19	34	232	2411	395	64.6%	255	945
6	55%	45%	2200	27	31	297	4241	670	63.8%	427.8	990
7	50%	50%	2500	25	24	301	3031	400	77.1%	308.4	990
8	50%	50%	2700	20	28	267	2504	570	83.5%	466	544

The variation was obtained by changing the composition of the charge, and the duration of time and energy supplied.

Voltage and current are given as an average, but the Watt hours represent the energy supplied. The yield is the weight of product obtained, this product had a variable composition so far as its content of CaC_2. This percentage is placed under product. The next column "actual carbide" gives the weight of

100 per cent. CaC_2 obtained, and the last the watt hours necessary to form 100 grams of pure carbide. That pure carbide is never obtained is seen by the fact that the actual percentage of CaC_2 varies in this work from about 39 per cent. to 85 per cent.

In order to compare the commercial product with that made in these experiments, samples of carbide obtained in the market were analyzed with the following results:

1st American sample.....65.66 per cent. carbide
2d American sample.....57.40 per cent. carbide
French candied carbide.....74.90 per cent. carbide

Conclusion.

In conclusion, the following points may be made:

1. The results obtained show that in all respects the resistance method is the most efficient. On an average the resistance method was about three times as efficient as the arc method, while the best run of the resistance method was twice as efficient as the best run of the arc method.

2. It was found that in both methods the quality of the yield was mainly influenced by the proportion of coke and lime used in the charge.

3. In the arc method, the best carbide was obtained with a charge of 55 per cent. coke and 45 per cent. lime. In the resistance method, the best carbide was obtained with a charge of 50 per cent. coke and 50 per cent. lime.

4. The time of run influenced the quantity of the yield, but after 8-9 minutes in the arc method and 20-22 minutes in the resistance method, the increase in yield is not proportional to the increase in length of run.

5. The value of the current used in the resistance method influenced the quality of the yield. If the current was too high it was found that it was burnt, due to excessive heat.

6. In the resistance method, the best part of the carbide was found at the bottom of the furnace, while that part directly between the electrodes was somewhat burned. This was due to the fact that the main part of the current passed through this part of the charge and the temperature reached was above that necessary for the formation of calcium carbide.

7. In the arc method, the best of the carbide was found at the bottom of the crucible.

8. An analysis showed that about 20 per cent. of the original coke in the charge was burned out of the unconverted charge in the resistance method.

Electrochemical Laboratory,
Columbia University,
February, 1909.

DISCUSSION.

DR. O. P. WATTS (*Communicated*): These experiments seem to me to have been conducted upon too small a scale, particularly as to time, for the results arrived at to be applicable to the manufacture of calcium carbide as carried on commercially. In addition, several of the conclusions enumerated at the end of the paper hardly seem to be warranted by the experiments described. V. B. Lewes, in his book, "Acetylene," pp. 242, 262, gives the yield of carbide at Meran and at Foyers as 5.8 kilos per kw. day, and 3.78 kilos per e.h.p. day. These values correspond to 513 and 473 watt hours per 100 grams of 100 per cent. carbide, so that commercial arc furnaces are more efficient than the resistance furnace used by Professor Tucker. May not the comparatively poor showing of the arc furnace in these experiments be due to the fact that it was about one-half the size, with one-tenth the charge, operated for one-third the time, and with a half to a third of the total energy used in the resistance furnace?

The fourth conclusion upon the relation between length of run and efficiency would seem to be based upon experiments not included in the paper, since eight to nine minutes, the length of run at which the efficiency of the arc furnace is said to begin to fall off, is the longest run recorded with this furnace. Lewes, p. 249, speaking of the arc furnace at San Marcello, which produces 300 to 500 pounds of carbide, says: "Having regard to efficiency, it would be more convenient to work more than five hours, as the production of carbide is larger during the last moments."

In the absence of samples of the carbide produced, the only discussion of the fifth conclusion must be from the data of Table II. The maximum difference of current for the same composition of charge was in runs No. 5 and No. 6, the average currents for which were 232 and 297 amperes, and the quality of carbide obtained was the same within the probable experimental error of the method of analysis used. Runs No. 1 and No. 2 show results contrary to the conclusions stated, leaving only runs No. 7 and No. 8 to support the conclusion stated.

Experiments by the writer agree with conclusion 6 as to the location of the best carbide. A run of an hour at 80 to 100 kw. resulted in a sheet of carbide 30 inches long; 5 to 7 inches wide, and 1 to 1½ inches thick, weighing 11 pounds. It was crystalline and uniform throughout, except that in places the top was contaminated by the granular carbon of the resistor. Its horizontal upper surface, and the fact that it was much wider than the original resistor, seemed to indicate that it had been fused. The great steadiness in the operation of the furnace electrically, during the latter half of the run, seemed to point to a fluid resistor rather than to one of granular carbon. It was therefore thought that the current was mainly passing through the carbide, rather than through what remained of the granular resistor above it. Professor Tucker has stated that on opening his furnace a solid mass of carbide was found connecting the furnace electrodes. This carbide when melted or when extremely hot would probably be a better conductor than the charge above it, so that the main current would pass through the carbide, and not directly between the electrode through the charge. May not the "burned" carbide between the electrodes have been that which was not hot enough to form good carbide, rather than the result of excess of heat? From an arc furnace operated at 50 to 60 kw. for an hour and a half, the writer obtained a single lump of crystalline carbide weighing 17½ pounds. This was uniform and did not appear burned.

Prof. S. A. Tucker *(Communicated)*: In answer to Dr. Watt's communicated discussion on the subject of carbide the experiments show clearly in favor of the resistance furnace on the scale on which they were conducted. It is unfortunate that the arc furnace was of even smaller capacity than the resistance

furnace, but at the time this could not be avoided. The probability is that in working on a large scale the so-called arc furnace operates on the resistance principle almost entirely, which would account for the higher efficiency quoted by Dr. Watts. The aim in this set of experiments was to compare the operation of an actual arc and resistance furnace, and I believe when an arc is used it results in a poor efficiency probably for the reasons named.

A paper presented at the Fifteenth General Meeting of the American Electrochemical Society, at Niagara Falls, Canada, May 8, 1909; President E. G. Acheson in the Chair.

FURTHER EXPERIMENTS WITH CALCIUM ALLOYS AS REDUCING AGENTS.

By O. P. Watts and E. R. Suhm.

At a previous meeting of this Society one of the members made a suggestion to the effect that an account of our failures might prove sometimes quite as helpful as an account of the successful researches usually described; so, although the results hoped for when these experiments were undertaken have not been realized, the methods used may perhaps be of value to others who are experimenting along similar lines.

The present paper is a continuation of one which appeared in Volume XIII of the Transactions of this Society, entitled "The Preparation of Calcium Alloys for Aluminothermic Work." In the few experiments tried at that time the reactions were violent and the yield of metal was small. One of the objects of the experiments about to be described was to suppress this violence of reaction.

Since the heats of oxidation per gram equivalent of calcium and of magnesium are greater than that of aluminum, and because in some proportions the mixed oxides melt at a lower temperature than pure alumina, it was expected that these alloys would prove more effective reducing agents than aluminum, and it was hoped that by their use it might be possible to obtain fused tungsten and titanium as reduction products.

Aluminum Versus Calcium-Magnesium-Aluminum Alloys as Reducing Agents.

At the outset a direct comparison was made between aluminum and an alloy consisting of 30 per cent. calcium, 20 per cent. magnesium, 50 per cent. aluminum in the reduction of a mixture of rutile and manganese dioxide in proportions calculated to yield

a manganese-titanium alloy containing 35 per cent. of the latter. Charges of 250 grams were fired in the usual way by magnesium ribbon surrounded by an igniter of barium peroxide and finely powdered aluminum. The granulated aluminum gave an excellent reduction and a good ingot of manganese-titanium alloy, but the reaction of the calcium alloy was very violent, blowing part of the charge from the crucible, and the resulting alloy was scattered through the slag in globules about the size of peas.

Substitution of External Heat for that Produced by the Reduction of Manganese Dioxide in the Previous Experiments.

Experiment 10: A charge of 90 grams pulverized rutile and 81 grams of the calcium alloy previously mentioned, without the igniter, was heated in a graphite crucible for twenty minutes in a resistor furnace, using 20 kilowatts. The reaction was quiet, but the yield was only 26 grams, or 48 per cent. of metal in scattered globules. The temperature had not been high enough for a good separation of metal and slag.

Experiment 11: The experiment was repeated on a larger scale, heating for 10 minutes by 24 kw. a charge of 281 grams of rutile and 255 grams of alloy. Twenty-seven grams of metal was obtained in globules, but much metal was scattered throughout the slag in particles too small for collection. Analysis of the product gave 75.3 per cent. titanium and 25 per cent. aluminum. This indicated that more than the theoretical amount of rutile is required in the charge in order to completely oxidize the aluminum, and accordingly more than the theoretical proportion of rutile was used in later experiments.

Experiment 13: Two hundred and forty-five grams of alloy was mixed with an amount of rutile 40 per cent. in excess of that required by theory, and the charge heated by 17.5 kw. for fifteen minutes. The resulting metal was scattered all through the slag.

Experiment 14: As a comparison, the same weight of rutile mixed with an amount of comminuted aluminum chemically equivalent to the alloy previously used, was heated by 19 kw. for thirty minutes. There was no outward manifestation of reaction, but reduction had occurred. The metal settled through the slag and collected in several large globules. This reduction by alumi-

num was more satisfactory than similar ones in which calcium alloys were used.

Experiment 15: In the hope of attaining a higher temperature, an alloy consisting of 60 per cent. calcium and 40 per cent. magnesium was tried upon excess of rutile. The reaction was quiet, although flames came from the crucible for thirty seconds. There was no separation of metal and slag.

It was evident that some way must be found of heating the charge considerably above the temperature at which reaction begins in order that the heat added by the reaction should produce a fluid slag and a good separation of metal. An attempt to add the charge to a crucible previously heated to whiteness resulted in the ignition of the charge before it got inside the crucible, and the consequent burning of the product in the air.

In this juncture an article read a dozen years ago upon the effect of size and shape of grain upon the rate of combustion of the brown prismatic powder used in large ordnance suggested a possible solution. As a result of experiments with grains of various sizes and shapes, and with perforations to increase the amount of surface, it was determined that the combustion of gunpowder is purely a surface phenomenon, and that the rate of combustion depends on the ratio of surface to mass.

In the previous paper upon calcium alloys the violence of reaction was ascribed to the sudden vaporization of a part of the calcium or magnesium before it could combine with the oxide which was being reduced. Attemps to use more finely pulverized materials and to secure more intimate contact betwen alloy and oxide had resulted in the blowing of most of the material out of the crucible. The use of briquettes promised to give a fairly slow reaction, even though the reducing agent and oxide were used in a very fine state of division.

The Use of Briquetted Charges to Diminish the Speed of Reaction.

An alloy consisting of 23 per cent. aluminum, 35 per cent. calcium and 42 per cent. magnesium was ground as fine as possible in a disc pulverizer, mixed with pulverized rutile, and made into briquettes using a 10 per cent. solution of gum arabic in

water as a binding material. The briquettes contained 10 per cent. of rutile in excess of the theoretical amount.

Experiment 17: A crucible of Acheson graphite with an electrically baked lining of magnesia was heated to whiteness in the resistor furnace and the briquettes added one at a time. They slowly settled in the crucible, but gave no other indication of reaction. As a result of this experiment there was on the bottom of the crucible a layer of very porous, yellowish metal, with slag above it, then another layer of metal. Near the top the briquettes could still be distinguished, each having a metallic core with slag on the outside.

The briquettes had proved satisfactory in suppressing the violence of reaction, but the temperature attained was still too low for a good separation of metal from slag.

Experiment 20: A similar experiment was tried using an alloy of the formula Al_2CaMg with the theoretical proportion of rutile. As binding materials solutions of gun damar, tragacanth, shellac and linseed oil were used. Graphite crucibles with magnesia linings were heated by 24 kw. for two hours before adding the briquettes. Reaction was quiet in each case. The briquettes made with gum damar gave sparks and some smoke, and those made with linseed oil gave off a thick black smoke for nearly a minute. The result was about the same as in experiment 17.

An attempt was now made to secure a higher temperature by adding to the charge a considerable excess of calcium alloy and enough barium peroxide to oxidize it, thus adding greatly to the heat of reaction, yet introducing no other metal into the product, as was done when manganese dioxide was used as the oxidizing agent. Briquettes were accordingly made of the alloy Al_2CaMg with 10 per cent. excess of rutile, to which different amounts of the heat-producing mixtures of alloy and barium peroxide were added.

(*a*) 60 per cent. charge and 40 per cent. heating mixture.
(*b*) 50 " " " " 50 " " " "
(*c*) 40 " " " " 50 " " " "

Experiment 21: A graphite crucible four inches in diameter and six inches high with a magnesia lining, was heated to white-

ness in the resistor furnace and the briquettes were dropped in one at a time. All reactions were violent, increasingly so in proportion to the amount of fuel and oxidizer added to the charge. The product was a white, porous metal of rather high density, but poorly separated from the slag.

An attempt was now made to obtain fused tungsten by the use of the same alloy as a reducing agent.

Experiment 22: Briquettes were made of Al_2CaMg and WO_3, using 15 per cent. of the latter in excess of the theoretical amount to insure complete oxidation of the reducing agents. Two charges were made into briquettes, using shellac as a binder.

(*a*) 171 grams WO_3 + 51 grams alloy.

(*b*) 103 grams of (a) + 103 grams of BaO_2 and alloy.

Two graphite crucibles with magnesia linings were heated to intense whiteness by 50 kw. At the end of forty-five minutes heating the briquettes were dropped in.

(*a*) The reaction was rapid, but not violent, and resulted in a single mass of tungsten. The metal had sintered rather than fused and was a mere shell, having the form and nearly the size of the original briquettes. The metal was entirely free from slag.

(*b*) The reaction was very violent and much material was projected from the crucible. The product was a porous mass of intermingled metal and slag at the bottom of the crucible. The magnesia linings were in good condition.

Experiment 23: An arc at 40 to 50 kw. was substituted for the resistor furnace in the hope of getting a higher temperature. Briquettes were made with shellac of 297 grams rutile and 172 grams Al_2CaMg. A graphite crucible four inches in diameter and six inches high was placed upon a slab of graphite, which served as one terminal, and surrounded by finely pulverized carbon. The bottom of the crucible was covered with a layer of magnesia to prevent contact of the reduced metal with carbon. The arc was started by laying a small carbon rod on top of the magnesia and bringing the upper electrode down upon it. Pure alumina was added and thoroughly fused. When the current was interrupted for the purpose of adding the charge, the alumina at once solidified. To prevent this, barium carbonate and lime were added and the whole fused by the arc. The circuit was

then broken and briquettes fed in until the slag began to freeze, when the arc was started again, and so on until all the charge had been added. On examining the crucible a few globules of metal were found resting on the magnesia bottom and well separated from the slag above. Half way up was a mixed mass of metal and slag, and near the top was a porous, reddish mass that appeared to be titanium nitride, with a thin layer of slag above it. The only good separation of metal and slag occurred at the outset when the original fusible slag was in large amount compared to the charge.

Adding the Charge to a Fused Slag.

In the hope of getting a better separation of metal a mixture of oxides was fused in the crucible and the charge dropped into the molten mass.

Experiment 24: Two Acheson graphite crucibles 4" x 6" with an inch of magnesia in the bottom were heated in the resistor furnace. Thirty-four hundred grams of a mixture having the composition $2CaO.BaCO_3.2Al_2O_3$ was prepared.

(*a*) The charge was composed of 65 parts of the mixed oxides to 35 parts rutile. When this was thoroughly fused, 100 grams of aluminum wire in a single piece 1/8" in diameter was slowly introduced into the crucible. There was a very marked increase in temperature and at times the slag boiled over the edge of the crucible. A thin layer of whitish metal was found at the bottom of the crucible. Its color would indicate that it contained aluminum alloyed with the titanium.

(*b*) $2CaO.BaCO_3.2Al_2O_3$ was fused and briquettes of 559 grams WO_3 + 149 grams Al_2CaMg were thrust into the fused mass. The reaction was violent, spattering fused slag several feet out of the furnace. There was no separation of metal. The product was dark gray and of high density.

Experiment 25: The reduction of rutile was tried on a larger scale. Twelve hundred grams of $2CaO.BaCO_3.2Al_2O_3$ was mixed with 800 grams of rutile and fused in the resistor furnace. Four hundred and fifty grams of aluminum wire was then added. After cooling, it was found that the layer of magnesia placed on the bottom of the crucible at the outset, had disappeared. A layer of titanium on the bottom had taken up carbon from the

crucible. Higher up in the crucible there was a considerable mass of white metal, which was found to consist of 80 per cent. titanium and 20 per cent. aluminum. This method fails to produce pure titanium because of the latter's affinity for aluminum.

Experiment 26: It is well known that the oxides of tungsten and molybdenum are volatile at high temperatures. This experiment was tried to see if the vaporization of MoO_2 could not be prevented by causing it to combine with other oxides before the highest temperature was attained. Accordingly 200 grams of MoO_2 was mixed with 1200 grams of $2CaO.BaCO_3.2Al_3O_3$ and the mass fused in a graphite crucible in the resistor furnace. No vaporization occurred. Six hundred grams more of MoO_2, which is 150 grams in excess of the aluminum added later, was mixed with the oxides of calcium, aluminum, etc., and gradually added to the fused mass in the crucible. Much vaporization occurred. Before all of this mixture had been added aluminum wire was fed in, then more mixture, and so on alternately until the whole 182 grams of aluminum had been added. On opening the crucible, 248 grams of a white, dense metal with a conchoidal fracture was found on the bottom of the crucible. The layer of magnesia which was placed in the crucible had disappeared. Above the metal was a layer of crystalline slag. The separation of metal and slag was perfect. The yield of metal was 51 per cent. of theory. A quantitative determination gave 99.5 per cent. of molybdenum. This experiment would seem to show that loss of MoO_2 and WO_3 by vaporization can be prevented by admixture with other oxides, provided the entire charge be put into the cold crucible and heated gradually.

Several additional experiments were tried in the direct comparison of the efficiency of aluminum and Al_2CaMg upon Mn_3O_4 according to the regular Goldschmidt method.

Experiment 27: (*a*) Sixty-four grams Mn_3O_4 + 26.4 grams alloy gave an excellent separation of metal from slag, and a yield of 43.4 per cent. of the theoretical amount of metal. The reaction was steady and quiet.

(*b*) Seventy-four grams Mn_3O_4 + 25.4 grams granulated aluminum gave a slow, quiet reaction, but a very poor separation of metal from slag.

(*c*) Two hundred and fifty-six grams Mn_3O_4 + 105.6 grams

alloy reacted quietly and yielded 70 grams of metal in a single ingot, a yield of 57 per cent. The metal was hard, dense, and resembled commercial manganese produced by the Goldschmidt process. The slag was greenish in color, showing a desirable amount of unreduced manganese oxide.

Experiments with Cr_2O_3 on a similar scale yielded only scattered globules of metal. This result is not surprising in view of the statement by L. Guillet[1], as a result of many experiments, that the reduction of Cr_2O_3 by aluminum is not successful in small charges up to 3 kilograms.

Summary.

The direct comparison of aluminum with the alloys as reducing agents gave conflicting results. In the reduction of a mixture of MnO_2 and TiO_2 aluminum was superior, while in reducing Mn_3O_4 the alloy gave far better results. It is probable that the alloys are superior in all cases where none of the charge is blown out of the crucible. The alloys are distinctly superior to aluminum for the igniting mixture.

Attempts were made to supply enough heat to secure solid masses of tungsten and titanium.

(a) by rapidly heating a charged crucible in a resistance furnace.

(*b*) by heating with an arc of 50-60 kw.

(*c*) by feeding the charge into a mass of melted oxides,

(*d*) by adding BaO_2 and extra alloy to the charge.

All these methods failed.

Molding a charge of very finely pulverized material into briquettes was very effective in suppressing too great violence of reaction.

The vaporization of MoO_2 can be prevented by getting it into combination with other oxides before an extremely high temperature is attained.

Since the violence of reaction of the alloys increases with the amounts of calcium and magnesium, the most serviceable, as well as the cheapest, alloys will probably be those with only enough calcium or magnesium to be readily pulverized.

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[1] Les Alliages Metalliques, p. 18.

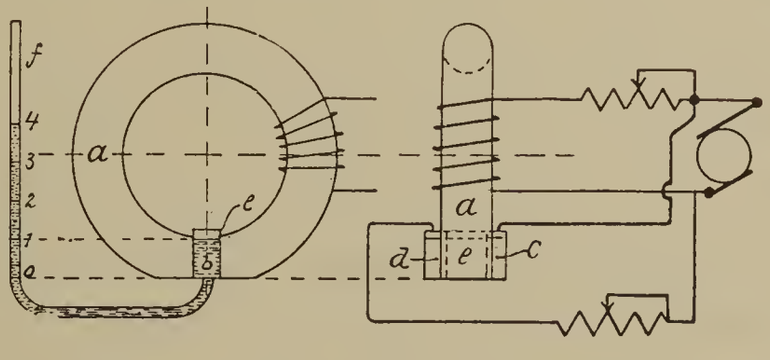
A paper presented by Mr. Carl Hering at the Fifteenth General Meeting of the American Electrochemical Society, at Niagara Falls, Canada, May 8, 1909; President E. G. Acheson, in the Chair.

ELECTROMAGNETIC SEPARATION OF NON-MAGNETIC, NON-CONDUCTING, SUBSTANCES.

By A. P. Steckel.

The method here described was the result of a study of the problem of obtaining a more thorough concentration of Lake Superior native copper ores. For several reasons given later the desired result was not fully realized, but the method is new and more or less interesting in view of its possible success under more favorable conditions.

Working on the reasonable assumption that a perfectly fluid liquid of proper specific gravity should furnish a key to the problem, by making possible the flotation of the lighter substance, regardless of size or shape of the particles, the writer cast about for such a liquid; but meeting with no success in the search, resorted to the following expedient, which, when worked through all its possible variations, may be said to give to any conducting liquid any desired specific gravity from zero upward.



In the adjoining diagram, *a* is an electromagnet in the gap of which is a trough, *c*, of uniform cross section, made of insulating material, and carefully leveled so that a liquid, *b*, partially filling the trough shall have uniform cross section. The liquid is water containing a few per cent. of sulphuric acid for the purpose of increasing its electrical conductivity. At the ends of

the trough, but purposely set somewhat inside the boundaries of the magnetic field, are carbon electrodes, *c* and *d*, accurately fitting the trough and carrying direct current to and from the liquid conductor. The relation between direction of magnetic field and direction of current in the liquid is such that the electromagnetic force brought to bear on the liquid is downward.

It was assumed in designing the apparatus that the liquid conductor carrying a given current across a field of given strength would be acted upon by a downward force in no wise different from that which would appear in a solid conductor under the same conditions.

To obtain a force of one gram per cubic centimeter of liquid, the product of field strength in lines per square centimeter and amperes per square centimeter should be 9,810. Since three grams were required in addition to the natural weight of the water to obtain a specific gravity of four, the above mentioned product had to be 3 x 9,810, or 29,430, hence the high field strength of 29,430 lines per square centimeter was aimed at, which necessitated the use of a current density of 1 ampere per square centimeter. It was found easier to obtain the required force by using a considerably weaker field and a correspondingly stronger current in the liquid.

The attachment, *f*, shown in the figure is a gauge glass for accurately observing the so-called specific gravity of the liquid. The number, 1, on the scale is at the level of the top of the liquid in the trough, and the spaces between numbers on the scale are equal to the depth of the liquid. Before attempting to use the apparatus in concentrating ore, various interesting experiments were performed, pieces of glass and of rock, as large as could be accommodated in the trough, being floated on the water. Specific gravities between 1 and 0 were obtained by reversing the direction of current and applying only enough current to partially balance the normal weight of the water. In this way pieces of wood were caused to sink or rise by closing and opening the circuit through the liquid.

As first constructed, the trough was 2 inches wide by 4 inches deep by 15 inches long. Although the performance above described was found possible with a trough of these dimensions, it was not possible to hold the liquid sufficiently quiet to even

attempt a treatment of finely divided material. A flotation process, especially if fine particles are to settle, requires a quiet liquid, but the liquid under the conditions described above was far from quiet. At first it was thought that the violent agitation of the liquid was due primarily to the rise of gas bubbles at the electrodes, but after this source of trouble had been eliminated by the use of porous woolen screens near the electrodes, the agitation of the liquid was still quite violent.

There was always a marked tendency of the liquid to become depressed at the middle of the length of the trough and to rise at the ends with a consequent flow. Although it was realized that at best the liquid was in an unstable condition, the persistent tendency to rise at the ends was attributed to weakness of field near the edges of the magnet poles due to end leakage. As a test of this point, the electrodes were moved in so that the body of liquid was only 6 inches long. When this change had been made, the liquid became quieter, and a small quantity of finely divided mixture of copper and rock (15 per cent. copper) was put into the liquid to test the scheme of concentration. The presence of this material increased the general agitation somewhat, but it was also noted that each particle of suspended material had an irregular motion of its own. Although all the large particles of copper went to the bottom and all the large particles of rock stayed at the surface, there was not a satisfactory separation of the fine particles either of copper or of rock; in fact, an assay of the tailings skimmed from the top showed 5 per cent. copper, all of which was composed of fine particles of copper not allowed to settle on account of the troublesome agitation.

Without going into details as to means provided for making the process continuous, changing the liquid rapidly enough to prevent boiling, precautions to secure uniformity of field density and current density, etc., it is sufficient to say that under the most favorable conditions, with a perfectly broken mixture of copper and rock assaying about 15 per cent. copper, the size of particles of both materials ranging from 0.06 inch to 0.001 inch diameter, the lowest proportion of copper in the tailings ever obtained was about 4 per cent.

This poor showing cannot be accounted for by the presence

of any great amount of extremely fine copper, for in perfectly still water only a few seconds were required for complete settling of the mixture.

Although the cost of power alone might seem a sufficient reason for abandoning the above scheme without a trial, the writer is sure that in the absence of certain unforeseen drawbacks the cost of power would not be prohibitive.

If a practically quiet condition of liquid could be maintained in a trough of considerable dimensions, the high degree of perfection of separation naturally to be expected from a device of this sort would fully warrant its first cost and operating expense, when the alternative involves great loss of valuable material in tailings or high smelting cost.

Exhaustive experiments led to the conclusion that where electromagnetic forces, as great as in the present instance, are necessary, the liquid cannot be held quiet enough for practical purposes.

The agitation was found to be of two kinds: One, a general movement of the liquid upward near the electrodes and downward midway between electrodes; the other, a local agitation in the neighborhood of each suspended particle. The former can be practically eliminated by employing transverse porous screens in the trough, or by using a narrow enough trough, both of which expedients stand seriously in the way of practical operation. The agitation in the neighborhood of each particle cannot be avoided, being inherent in the scheme. It is explained as follows: Since non-conducting (and even conducting particles when sufficiently small) do not participate with the liquid in carrying current, there is a space immediately ahead of and immediately behind every such particle, in the direction of flow of current, in which no current flows. The liquid in these small spaces, hence, has only ordinary weight, with the result that an eddy is formed which tumbles the particle around in an irregular manner, making its floating or sinking a matter of uncertainty, but making floating more probable, because the eddy is upward at both ends of the particle. This trouble becomes more of a factor the smaller the particle.

The experiments described were carried on by the writer at the Buffalo Smelting Works, during the years 1905, 1906 and 1907.

DISCUSSION.

PROF. H. K. RICHARDSON: How large a particle was used?

MR. CARL HERING: The size of the particle has nothing to do with it. It is a question of specific gravity only. For instance, a piece of glass almost as large as the cloth will float as well as a small piece. There is, however, this exception: If you put a short piece of aluminum on the surface of that liquid it will float, even though it is quite large and bulky; but a long, thin aluminum wire will sink, because the drop of potential between the ends is then great enough to send the current through the wire, and, of course, the moment the current passes through the wire, it will sink; with a short piece the drop of potential is not enough to overcome the terminal voltage.

PROF. J. W. RICHARDS: I would like to ask Mr. Hering whether the force which causes this phenomenon is similar to that which causes the liquid metal in an induction furnace to tend to rise, so that sometimes it will rise clear from the bottom of the trough and remain suspended simply in the space above the supporting bottom of the trough.

MR. HERING: I could not answer that offhand, but there is a difference between the trough of Mr. Steckel and that of the induction furnace, insofar that in the former there is a strong external magnetic field, while in the latter this field is very much weaker and may have a different relative direction. The resulting action, of course, depends upon the direction of the field and especially on its strength. The field has to be crosswise very intense in Mr. Steckel's trough. You can get some idea of the field he used from the fact that the core weighed a ton, and the copper around the outside of the field also weighed about a ton.

PROF. J. W. RICHARDS: Mr. Chairman, I do not like the expression so frequently used in the paper, "increasing the specific gravity" of the liquid. I think it is misleading, even though it is added that it is only an "apparent" increase of specific gravity. There is certainly no increase of the specific gravity of the liquid, but merely a tendency of the liquid to

move away from the non-conducting particles which are in it, or *vice versa.* I have formed a conception in my mind, which may not be exact, but which has made the action somewhat clearer to me, and that is to compare it to the centrifugal action in a centrifugal separator, where you apparently increase the difference in the specific gravity of things by means of the centrifugal force.

Mr. T. J. Hancock: I would like to ask if the current through the channel was alternating or direct?

Mr. Hering: The current must, of course, be direct. It could not be done with an alternating current, unless you had an alternating current magnet that was exactly in phase with it.

Mr. Hancock: That was what I was thinking; but if it was direct current there would be polarization somewhere.

Mr. Hering: There is polarization, of course, at the electrodes, but the agitation due to the gassing was easily prevented by the porous diaphragm in front of the electrodes.

A paper read at the Fifteenth General Meeting of the American Electrochemical Society, at Niagara Falls, Canada, May 7, 1909; President E. G. Acheson in the Chair.

THERMODYNAMICS OF THE WESTON STANDARD CELL.

By G. A. Hulett.

E. Cohen[1] has considered the question of the thermodynamics of the Weston standard cell. The Gibbs-Helmholz equation $E = Q + T\frac{dE}{dT}$, gives a means of calculating the algebraic sum of the heat of all reactions which take place when the cell is giving a current. The e.m.f. and temperature coefficient of the cell at 18° were taken as 1.0186 volts and —0.0000354 per degree. From these determinations Cohen calculated the effective heat the reactions as 46,880 calories (47,880 calories given in the article, but this is probably a misprint).

The cell is constructed as follows:

Cadmium amalgam/$CdSO_4$ $8/3H_2O$,Hg_2SO_4/Hg,

and it is seen that cadmium sulphate is formed at the anode (+219,900 calories) and mercurous sulphate decomposed at the cathode (—175,000 calories), but the difference (44,900 calories) does not correspond to the calculated value, and Prof. Cohen has pointed out that not $CdSO_4$ but the hydrated salt was formed and the water was taken from the saturated solution. This heat he found to be +7,822 calories, and this with the 44,900 gave 52,722 calories, which is also not in agreement with the calculation, and for the reason that cadmium sulphate is formed not from cadmium but from the cadmium of the two-phase amalgam, and the heat needed for this transference was obtained thermodynamically from the combination:

Cadmium amalgam/cadmium sulphate solution/cadmium,

which was found to have an e.m.f. of 0.04993 volts at 25° and

[1] Zeit. Phys. Chem., **34**, 612.

a negative temperature coefficient of 0.000233. A calculation showed that in transferring cadmium to the two-phase amalgam, 5,436 calories were liberated, and this was to be taken as negative in determining the effective heat of the reactions in the Weston cell, and thus the sum was 47,286 calories, as compared to the 46,880 calories calculated.

Our interest in this question centers principally upon the calculated difference of heat energy between metallic cadmium and cadmium in the two-phase amalgam. Prof. Cohen used a 14.3 per cent. amalgam in his combination, cadmium amalgam/cadmium sulphate/cadmium, and from the work of H. C. Bijl[2] it appears that this is very near to the composition which forms only a solid phase at 25°, and is surely not two-phase below this temperature. It is probable that both the e.m.f. and temperature coefficient observed by Prof. Cohen were too low. In a previous article[3] the author made a study of this combination, using 12.5 per cent. amalgam and various concentrations of electrolyte, and as the anode cadmium in various forms. It was found that the e.m.f. of this combination at 25° was 0.05053, with a temperature coefficient of — 0.000244. Many of these cells are still in good order after five years, and lately more have been made, but with 10 per cent. amalgam for the cathode. These cells were found to agree exceptionally well for a cell with a solid as an electrode, and their values have been determined at intervals of 5° from 15 to 40°. Baths were used which were constant to 0.01° at the various temperatures and for any desired period; generally the cells were observed for a week or ten days at one temperature. The temperature coefficient of this combination is linear and —0.0002437. The e.m.f. of the different cells varied somewhat in value, due to the cadmium electrode. The cadmium was deposited electrolytically on a platinum spiral after the cell was constructed, and was generally beautifully crystalline, but in some cases it was spongy. The reproducibility seemed to be about 0.5 millivolt, and the most probable value at 25° was 0.05047, so we have for this combination $E_t = 0.05047 - 0.0002437\ (t - 25)$, and applying the Gibbs-Helmholz equation to this cell we find $Q = [0.05217$

[2] Zeit. Phys. Chem., **41**, 641.

[3] "A Low-Voltage Standard Cell," Transactions Amer. Electrochem. Soc., **7**, 333.

$+(291 \times 0.0002437)] \times 2 \times 23{,}046 = 5{,}674$ calories. This seems a surprisingly large amount of heat in view of the fact that the heat of amalgamation of cadmium is only about 500 calories.[4]

It is to be noted that the composition of the two-phase electrode changes with the temperature, and the question as to whether the Gibbs-Helmholz equation contemplates such a change in arriving at the temperature coefficient of a cell, is to be considered. It was thought that some evidence might be gained from the following considerations: If we start with the combination at 25°, where the e.m.f. is 0.05047, and remove the solid phase, we may, by proceeding to higher temperatures, obtain the temperature coefficient which will allow a calculation of the heat liberated when cadmium is transferred to the liquid phase of the two-phase amalgam. This temperature coefficient was found to be +0.000133, and a calculation showed that in transferring a gram atom of cadmium to the liquid phase of the two-phase amalgam at 25°, 500 calories were liberated. Now, if we start from 25° with the solid phase only as one electrode, and proceed to lower temperatures, the temperature coefficient obtained will allow of a calculation of the heat liberated in transferring cadmium to the solid phase, and the difference between this value and the one just obtained must represent the heat liberated in transferring cadmium from the liquid to the solid phase. A 20 per cent. amalgam was slowly cooled at 25° and maintained for several days at this temperature. By means of a centrifuge it was found possible to make an exceedingly effective separation of the liquid from the solid phase, and this latter was used in two cells with a saturated cadmium sulphate solution and cadmium anodes. The cells were maintained constantly at 0° C. for several weeks before a constant value was obtained. The temperature coefficient was —0.000188. With 0.05047 as the 25° value of the cell this gives a calculated 4,984 calories as the heat liberated in transferring cadmium to the solid phase of the two-phase amalgam, and the difference between the two is 4,484 calories. When we dissolve a gram atom of cadmium in the two-phase amalgam, more than a gram atom of cadmium separates in the form of a solid solution with mercury, the liquid contains

[4] Richards and Lewis, Zeit, Phys. Chem., 28, 1.

5.6 per cent. of cadmium and the solid phase 15.3 per cent., so that about 1.45 gram atoms of cadmium separate from the liquid phase for every gram atom dissolved in it, and this would give us a liberation of 1.45 × 4,484, or 6,500 calories. The solid phase is an isomorphous mixture, and there were indications that it was not stable at 0°, so not much reliance can be placed on the temperature coefficient obtained, and for this reason the method is not an exact one for gaining the information desired. If the heat indicated by the Gibbs-Helmholz equation is liberated when cadmium is dissolved in the two-phase amalgam, it should be possible to directly measure the cooling effect of dissolving the solid phase in mercury, and this experiment is being tried.

As far as the Weston standard cell is concerned, it may be pointed out that it is not necessary to make the calculation, for we can combine the e.m.f. and temperature coefficient of this small cell directly with that of the standard cell and get the e.m.f. and temperature coefficient of the combination cadmium/$CdSO_4$ $8/3H_2O$ Hg_2SO_4/Hg. For example, the cell with three electrodes cadmium/$CdSO_4$/cadmium amalgam/$CdSO_4$ Hg_2SO_4 /Hg gives all possible combinations by measuring any two.

The most probable value of the Weston standard cell at 18° is 1.0185 volts, and Dr. F. A. Wolff has lately determined the temperature coefficient of this cell with great accuracy: $Et = 1.0184 - 0.00004075\ (t - 20) - 0.000000944\ (t - 20)^2 + 0.0000000098\ (t - 20)^3$, and on differentiation this gives $\frac{dE}{dT} = -0.00004075 - 0.000000944 \times 2 \times (t - 20) + 0.0000000098 \times 3 \times (t - 20)^2$ and $\left(\frac{dE}{dT}\right)_{18} = 0.000036866$. Combining with this the value of the small cell at 18° (+0.052176 with a temperature coefficient of —0.002437) we get for the Weston cell with a cadmium electrode at 18°, the value 1.07067 with a temperature coefficient of —0.0002806 and from $Q = E - T\frac{dE}{dT}$ we calculate $[1.07067 + (291 \times 0.0002806)] \times 2 \times 23{,}046 = 53{,}574$ calories, while the calorimetric value of the effective reactions was found to be 52,722 calories.

DISCUSSION.

MR. CARL HERING: Mr. Chairman, it has sometimes occurred to me, with the accuracy of modern methods of measuring voltages, whether it might not be more accurate to determine the heats of combination by the electrical method than to determine them directly. It seems to me it is easier to make electrical measurements very accurately than it is to measure the quantity of heats very accurately.

PROF. G. A. HULETT: It would seem so, Mr. Chairman, but the real difficulty is in the experimental determination of the temperature coefficient. It is not an easy matter to determine these temperature coefficients with sufficient accuracy even when they are linear functions of the temperature. The number sought is the small difference of two observations, and contains the errors of both observations, and thus may have a very considerable percentage error. In addition to this, the temperature coefficient is multiplied by the absolute temperature, and this multiplies the error by some 300. It is quite possible that in many cases one may get a more reliable temperature coefficient by reversing the process and calculating it from the calorimetric value of the reactions, using the Gibbs-Helmholz equation.

A paper presented at the Fifteenth General Meeting of the American Electrochemical Society, at Niagara Falls, Canada, May 7, 1909; President E. G. Acheson in the Chair.

THE FUNCTION OF ADDITION-AGENTS IN ELECTROLYTES.[1]

By Edward F. Kern.

The production of smooth, solid, coherent electrodeposits is of the greatest importance in the art of electroplating, and is much desired in the electrolytic refining of metals. One of the means which is practiced in order to accomplish this, is to add to the electrolyte certain reagents, which cause the deposit to form more dense, less crystalline, and smoother. The materials which are added to electrolytes for the purpose of improving the electrodeposits will be designated in this article as addition-agents.

Abstract of Literature.

In reviewing the literature on this subject, it was found that very little had been systematically and scientifically done in this field. Most of the data found were such as seemed to have been accidentally acquired in the art of electroplating, and were given somewhat after this manner: A certain reagent added to a certain electrolyte improved, or else "sickened," the deposit. The literature on electroplating contains considerable data of this nature for producing dense, smooth deposits, but in most cases such data are so incomplete, or else so misleading, that the production of satisfactory electroplates, by following the methods as given, is generally a matter of chance.

The addition-agents which have been found to cause electrodeposits of copper, lead, silver, nickel and iron to form more dense and more coherent are the following:

A. Copper Sulphate Electrolyte. A small amount of benzoic acid added to the electrolyte causes the copper to form as a

[1] This article is an expansion of articles which were published in the "School of Mines Quarterly," and which were based upon investigations conducted in the Metallurgical Laboratory of the School of Mines, Columbia University.

more tough and a brighter deposit;[2] 10 grams of glue per liter of acid copper sulphate electrolyte improves the deposit;[3] oak-wood tea, an extract of oak-wood, and which is composed chiefly of tannic acid, when added to the electrolyte causes the deposition of harder and smoother copper;[4] the presence of hydroxylamine in the electrolyte gives a more coherent deposit of copper.[5]

M. Kiliani[6] studied the effect of the presence of inorganic salts on the character of copper deposited from copper sulphate electrolytes. He noted the fact that the presence of a tin salt in the electrolyte caused the copper to deposit as a smooth, malleable sheet, whereas when no tin salt was present, the deposit of copper was exceedingly rough and brittle.

B. (a) Lead Fluo-silicate Electrolyte. The presence of a small amount of gelatine, glue, pyrogallol, resorcin, saligenin, orthoamido-phenol or hydroquinone causes the lead to deposit dense, smooth and coherent, which if one of the reagents were not present, would form crystalline and non-coherent.[7]

(b) Lead Nitrate Electrolyte. The addition of pyrogallol or hydroquinone to the electrolyte improves the deposit of electrolytic lead.[8]

C. (a) Silver-potassium Cyanide Electrolyte. The addition of carbon bi-sulphide causes the silver to deposit harder and brighter.[9] C. H. Porter found that benzol is a more suitable agent than carbon bi-sulphide, when added in the proportion of one teaspoonful per each gallon of plating solution.[10]

(b) Silver Methyl-sulphate Electrolyte. The presence of a small amount of either carbon bi-sulphide, gelatine, or gum arabic, reduces the size of crystals of the deposited silver, and also increases its coherency.[11]

(c) Silver Nitrate Electrolyte. The addition of one part of

[2] Metal Industry (1903), p. 179.
[3] Trans. Am. Elect. Chem. Soc., 6, 33.
[4] Trans. Am. Elect. Chem. Soc., 8, 83.
[5] Trans. Am. Elect. Chem. Soc., 6, 29.
[6] Berg und Huttenmann Zeit. (1885), p. 249.
[7] Bett's "Lead Refining by Electrolysis" (1908), pp. 14, 15, etc. Trans. Am. Inst. Min. Eng., 34, 175. Trans. Am. Elect. Chem. Soc., 8, 64.
[8] Zeit. Electrochemie, 7, 381 (1900); 9, 267 (1903).
[9] Trans. Am. Elect. Chem. Soc., 8, 83.
[10] Metal Industry, March (1909), p. 96.
[11] Bett's "Lead Refining by Electrolysis" (1908), p. 166; Elect. Chem. and Met. Ind., 3, 145 (1905); Trans. Am. Elect. Chem. Soc., 8, 122.

glue or gelatine to 5,000 to 10,000 parts of electrolyte, restrains the large cathode crystals of silver and increases their coherency.[12]

D. Nickel Electrolytes. The electrolytes which have been used for electroplating are: Nickel-ammonium sulphate, nickel-ammonium chloride, nickel-potassium cyanide, and nickel-ammonium phosphate, which in some cases contained varying amounts of one or more other chemicals, such as boric acid, phosphoric acid, citric acid, benzoic acid, tannic acid, acetic acid, tartaric acid, or the alkali salts of these.[13] The electrolyte which is in most general use is a slightly acid solution of nickel--ammonium sulphate, the acidity being due to the presence of a sufficient amount of a weak acid, such as benzoic, acetic, citric, tannic, tartaric, phosphoric or boric acid, which prevents the formation of insoluble basic salts. The presence of boric acid not only prevents the formation of basic salts but also causes the deposit to form smoother and less brittle, when the electrolyte contains from 0.3 to 3.8 grams H_3BO_3 per 100 c.c. solution.[14]

A means which has been taken to reduce the e.m.f. required for electroplating from the double sulphate electrolyte is the addition of sodium chloride, 5 to 10 grams per 100 c.c. solution, which, it is claimed, renders the deposit tougher, more reguline, and more adherent, as well as increasing the conductivity of the electrolyte.[15]

D. H. Browne, in an article[16] entitled "Nickel Cathodes," states that one of the difficulties encountered by all who attempt to produce sheets of nickel thicker than electroplates, is the tendency of nickel deposits to crack and curl from the cathodes. The art of producing solid adherent deposits of almost any desired thickness consists in carefully controlling and maintaining initially good conditions to the end, such as concentrated pure neutral electrolyte, circulation of electrolyte, constant current density, and constant temperature (better results obtained between 50° and 70° C.). The advantages gained by using an electrolyte consisting of the more soluble nickel chloride or nickel sulphate,

[12] Trans. Am. Elect. Chem. Soc., 8, 128.

[13] A. Watts, "Electro-Deposition" (1889), pp. 280-330. W. G. McMillain, "Treatise on Electrometallurgy" (1899), pp. 236-249.

[14] W. G. McMillian, "Treatise on Electrometallurgy" (1899), pp. 239 and 242. Metal Industry, Feb. (1909), p. 59.

[15] A. Watts, "Electro-Deposition," p. 326.

[16] Elect. Chem. and Met. Ind. (1903), **1**, 348. Mineral Industry, **13**, 342.

rather than that of the less soluble double sulphate, is strongly emphasized. The conditions which were found to give the best, most flexible and most adherent sheets of nickel from a chloride electrolyte were: Neutral solution containing 7 grams $NiCl_2$ and 18 grams NaCl per 100 c.c.; temperature of 60° to 70° C.; C.D. of 10 to 20 amperes per square foot; and efficient circulation.

Adams[17] found that it was impossible to electroplate homogeneous, adherent deposits of nickel from solutions which contained even a trace of nitric acid, whereas from solutions similar in composition, with this exception, the deposits were satisfactory.

E. Iron Electrolytes. Previous to 1880 the electrodeposition of iron was applied technically to electroplating iron upon the surface of engraved copper plates, in order to obtain a hard facing from which a greater number of sharp prints could be made. The electrolytes used were principally solutions of ferrous sulphate, containing varying amounts of either magnesium sulphate, ammonium sulphate, ammonium chloride, potassium-sodium tartrate, or else a mixture of two or more of these.

One of the difficulties experienced with all iron electrolytes was the ease with which the iron was oxidized, forming a brown precipitate of basic salt. This was retarded by some electroplaters by adding glycerine, and from time to time, as occasion demanded, sufficient acid to clear the solution. The presence of magnesium sulphate was found to cause smoother deposits, and also to decrease the e.m.f. The anodes were either wrought iron or steel plates.[18]

Burgess and Hambuechen produced smooth deposits of iron by using a neutral ferrous sulphate solution, containing ammonium sulphate. The electrolysis was conducted at a C. D. of 6 to 10 amperes per square foot, and with an e.m.f. of about 1.0 volt, the temperature of the electrolyte being about 30° C. The current efficiency was approximately 100 per cent. The iron deposited as a smooth, dense crystalline, brittle mass.[19]

S. Maximowitsch, St. Petersburg, Russia, claims to have obtained flexible solid deposits of iron by using a neutral electrolyte containing ferrous sulphate, sodium sulphate, magnesium

[17] School of Mines Quarterly (1902) **23**, 267.

[18] W. C. McMilliams' Treatise on Electrometallurgy (1899), pp. 251-258.

[19] Elect. Chem. Ind. (1904), p. 183. Trans. Am. El. Chem. Soc. (1904), **5**, 201. Elect. Chem. and Met. Ind. (1906), p. 225.

sulphate, and from 0.2 to 0.3 per cent. of ferrous bi-carbonate.[20] This was prepared by adding sodium bi-carbonate to a solution containing 20 per cent. of $FeSO_4.7H_2O$ and 5 per cent. $MgSO_4.7H_2O$, until a permanent white precipitate was formed, and which soon changed to a brown color, due to oxidation by the air.

Sherard Cowper-Coles invented a process in connection with an apparatus for electrolytically producing bright, smooth iron deposits in the form of tubes, sheets and wires.[21] The electrolyte is a neutral solution of ferrous sulfo-cresylate, which is prepared by saturating a 20 per cent. solution of sulfo-cresylic acid with iron. The electrolysis was conducted with a C. D. of about 100 amperes per square foot, and at an e.m.f. of 3.25 volts, when the distance between the electrodes was half an inch, and the temperature 70° C. Cathodes rapidly revolved.

Effect of Temperature, Current Density, Etc.

Not only is the deposit of metals affected by the presence of reagents in the electrolyte, but the temperature and the percentage composition of the electrolyte, the circulation of the electrolyte, and the current density at the cathode, all have a decided influence on the character of the deposit. The investigation of Foerster and Siedel[22] may be cited to show what effect the temperature of the electrolyte has upon the properties of electrolytically deposited copper. They found that the deposits which formed, when the electrolytes were at 40° C., were of uniform fine-size crystals, and fairly ductile; when the electrolytes were maintained at 60° C. the crystals were larger and the deposits less ductile than when formed at 40° C. By operating with the temperature of the electrolytes above 60° C. the tensile strength of the deposits was higher than the deposits formed in electrolytes at lower temperatures.

Experiments conducted by Von Huebl[23] for the purpose of determining the effect of current density upon the tensile strength of electrolytically deposited copper, ascertain that both the tensile

[20] Zeit. f. Electrochemie, Jan. 20 (1905); Elect. Chem. and Met. Ind. (1905), p. 115.

[21] London Electrical Engineering, June 13 (1907); Elect. Chem. and Met. Ind. (1907), p. 291.

[22] Zeit, für Electro-chemie (1899), 5, 508.

[23] Mitth. des k. u. k. Militargeorge Inst. (1886), 6, 51.

strength and the hardness of the deposited copper increased with the increase in current density up to about 28 amperes per square foot, independently of the percentage composition of the copper sulphate electrolyte.

A number of other references on the effect of current density, percentage composition and temperature of the electrolyte upon the properties of the deposited metal could be given, but as these references have no direct bearing upon the subject it is thought best to leave them out.

EXPERIMENTATL: PART I.[24]

A general statement may be made that the conductivity of an electrolyte varies directly as the weight of salt in solution, and the more concentrated the electrolyte, the more satisfactory the deposit. Another great advantage gained by using an electrolyte containing the more soluble salt is lessening the inconvenience due to salts crystallizing and collecting between contacts, and also forming on the electrodes, especially the anode, all of which offers high resistance to the passage of the current. So, before deciding on what salts would be used in the investigations, their solubility was looked up, and in most cases the most soluble were used in preparing the electrolytes.

The electrolytes which were selected for copper, lead and silver were:

1. Cupric sulphate, cuprous chloride, and cupric fluo-silicate.
2. Lead nitrate and lead fluo-silicate.
3. Silver nitrate and silver fluo-silicate.

The addition-agents tried with these electrolytes were:

(*a*) Gelatine, a complex protein material; the chemical arrangement of its constituents not entirely known; mainly an anhydride of amino-acids.

(*b*) Resorcinal, $C_6H_4(OH)_2$, meta-di-hydroxy-benzene.

(*c*) Pyrogallol, $C_6H_3(OH)_3$; 1, 2, 3 tri-hydroxy benzene.

(*d*) Tannin, $C_{14}H_{10}O_9$; the arrangement of the radicals of this compound is not known; it may be consideted di-gallic acid, gallic acid being $C_6H_4(OH)_3COOH$, tri-hydroxy benzoic acid.

[24] School of Mines Quarterly, 30, 100-129, Kern and Janis.

Preparation of the Electrolytes.

The electrolytes, with the exception of the fluo-silicates, were prepared by dissolving a known weight of the salts in water, adding a calculated amount of the respective acid, and diluting to such a volume as to give solutions which contained the desired amount of metallic salts and free acid.

Lead fluo-silicate electrolyte was made to contain about 10 grams of lead, as $PbSiF_6$, per 100 c.c. and a half molecular equivalent of free fluo-silic acid (3.4 grams H_2SiF_6 per 100 c.c. solution), by adding a weighed amount of white lead ($2PbCO_3Pb(OH)_2$) to a measured volume of the fluo-silicic acid solution. Before using the solution it was filtered.

The copper fluo-silicate electrolyte was prepared to contain about 6 grams of copper as $CuSiF_6$ per 100 c.c. and a quarter molecular equivalent of free acid (5.5 grams H_2SiF_6 per 100 c.c. solution) by dissolving a weighed amount of ignited pure cupric oxide in a measured volume of the fluo-silicic acid solution, in the proportion represented by the equation

$$H_2SiF_6 + CuO = CuSiF_6 + H_2O.$$

Five-fourths this quantity of acid was taken, giving the desired excess.

Silver fluo-silicate electrolyte was made to contain about 4 grams silver (as Ag_2SiF_6) and 0.67 gram free fluo-silicic acid per 100 c.c. (one-quarter molecular equivalent of free acid). It was prepared in the following manner: Forty grams of pure metallic silver was dissolved in a slight excess of nitric acid, the solution evaporated to dryness, and the mass treated with about 200 c.c. distilled water. To the solution was added a slight excess of a strong solution of sodium carbonate, which precipitated the silver as carbonate. The precipitate was washed by decantation, until free of sodium salts, and then a measured volume of the fluo-silicic acid added to the same beaker containing the precipitate. Reaction:

$$H_2SiF_6 + Ag_2CO_3 = Ag_2SiF_6 + H_2O + CO_2.$$

Five-fourths this quantity of acid was used, giving the desired amount of free acid present. By diluting to one liter the solution contained 4 per cent. silver and 0.67 per cent. free acid.

The Electrolysis.

The electrolyses were conducted in No. 2 and No. 3 beakers, the electrodes being strips cut from sheets of the pure metal; the size, in the case of the copper and the lead cells, was 2.5 by 3.3 inches. A mark was scratched on the cathodes at such a height (2.5 inches from bottom) as to give the desired current density, when the current was on. The distance between the anode and the cathode, in each cell, was one inch, and was maintained as such by wooden spanners, which were wooden strips with two parallel notches sawed one inch apart, and into which the electrodes were secured. The current was supplied by a battery of storage cells, and properly regulated by means of rheostats.

I. Lead Electrolytes, Which Contained no Addition-Agent.

The first set of 12 experiments were conducted with lead nitrate and lead fluo-silicate electrolytes; the six lead nitrate electrolytes contained 10 grams lead and 1.46 grams free nitric acid per 100 c.c. (one-quarter molecular equivalent of free acid), and the six lead fluo-silicate electrolytes contained 10 grams lead and 3.4 grams free fluo-silicic acid per 100 c.c. (one-half molecular equivalent of free acid).

The runs were made in sets of three cells each, connected in series. The temperature of the electrolyte in one cell of each set was held at about 20° C., that in the second cell at about 40° C., and that in the third cell at about 60° C. The temperature was kept constant by means of water-baths.

The current density employed for one series of runs (three nitrate cells and three fluo-silicate cells) was 10 amperes per square foot, and for the second series of runs was 30 amperes per square foot. In all cases the deposit formed as loosely adherent, bright, dendritic crystals.

The average e.m.f. of the nitrate cells with a C. D. of 10 amperes per square foot was: At 20° C. = 0.22 V., at 40° C. = 0.20 V., at 60° C. = 0.18 V.; with a C. D. of 30 amperes per square foot, it was: At 20° C. = 1.35 V., at 40° C. = 0.84 V., and at 60° C., = 0.64 V.

The average e.m.f. of the fluo-silicate cells, with a C. D. of 10 amperes per square foot was: At 20° C. = 0.18 V., at 40° C. = 0.16 V., at 60° C. = 0.13 V.; with a C. D. of 30 amperes per square foot, it was: At 20° C. = 1.35 V., at 40° C. = 0.84 V., and at 60° C. = 0.39 V.

The results of this set of experiments showed that the free acid in the nitrate electrolytes chemically attacked the electrodes, liberating nitrous oxide; and the higher the temperature of the electrolyte, the more vigorous the action. With the fluo-silicate electrolytes, the chemical action of the free acid on the electrodes was less apparent, even though there was present twice the chemical equivalent as was in the nitrate electrolytes.

The deposits from the fluo-silicate electrolytes were more adherent, and were composed of shorter crystals than those formed in the nitrate electrolytes.

As to the effect of current density upon the character of the deposits, it was found that with higher current density the deposit formed less coherent and was composed of longer and more easily detached crystals. With rise of temperature the effect of higher current-density was partially counteracted, that is, the deposits which formed at 60° C. were composed of shorter crystals, which were more coherent, and which adhered more strongly to the cathode than the deposits which formed at 20° or at 40° C.

II. Copper Electrolytes, Which Contained no Addition-Agent.

This series of experiments was conducted with cupric sulphate, cupric fluo-silicate, and cuprous chloride electrolytes; the composition of each was:

(*a*) The cupric sulphate electrolyte contained 16 grams cupric sulphate ($CuSO_4.5H_2O$) and 4 grams free sulphuric acid per 100 c.c. solution, or 4.1 grams copper and two-thirds molecular equivalent of free acid.

(*b*) The cupric fluo-silicate electrolyte contained 6.34 grams copper, and 3.6 grams free hydro-fluo-silicic acid per 100 c.c. solution (an excess of acid in proportion to one-quarter molecular equivalent).

(*c*) The cuprous chloride electrolyte was prepared to contain

1.7 grams copper as cuprous chloride, and 15 grams sodium chloride per 100 c.c. solution, which is a saturated solution of cuprous chloride in a 15 per cent. solution of sodium chloride. No free acid present.

The electrolysis was performed with sets of three cells, connected in series, but at three different temperatures; one cell was at 20° C., one at 40° C., and the third at 60° C., in order that the effect of temperature upon the deposition could be determined.

The current density used in one series of runs was maintained at 10 amperes per square foot, and another series at 50 amperes per square foot. The surface of the electrodes exposed to action was, in all cases, 2.5 by 2.5 inches, or 6.25 square inches. The distance between the electrodes was one inch.

The deposits formed in the sulphate and the fluo-silicate electrolytes, when the electrolyses were conducted at a current density of 10 amperes per square foot, were smooth, bright, solid and coherent in each case, whether the temperature of the electrolyte was at 20°, 40° or 60° C. The deposits formed in the fluo-silicate electrolytes were more bright and less crystalline than those formed in the sulphate electrolytes. The total time of the electrolysis was 310 minutes (5 hours and 10 minutes).

The theoretical amount of copper deposited during these runs, the electrochemical equivalent of copper being 0.3294 mg., was 1.952 grams. Comparing the weights of the copper actually deposited, the cathode gain in each case, when the electrolytes were at a temperature of 20° and 40° C., approximated the theoretical amount; but when the temperature was 60° C. the cathode gain was considerably less than theory. This discrepancy in the weights of the deposits formed in the electrolytes at 60° C. is due to chemical corrosion of the cathodes along the line of contact of the electrolyte and the atmosphere, which corrosion did not occur with the electrolytes at lower temperatures.

In order to better compare the character of the deposits formed in sulphate and in fluo-silicate electrolytes, and also to determine the effect of the temperature upon the deposition, a series of cells were electrolyzed at a current density of 50 amperes per square foot. The total time of the electrolysis was 460 minutes (7 hours and 40 minutes). The theoretical amount of

copper deposited was 14.782 grams. The average cathode gain was 15.71 grams; the agreement in the cathode gain of this set of experiments is close, especially when the electrolytes were at 20° and 40° C. The deposit formed in the sulphate electrolyte at 60° C. weighed less, due to chemical corrosion. The lower calculated weight of the copper deposited is accounted for by the error in reading the ammeter, and the length of time of the run, which magnified the error.

The average e.m.f. of the sulphate cells, with a C. D. of 10 amperes per square foot was: At 20° C. = 0.29 V., at 40°C. = 0.20 V., at 60° C. = 0.16 V.; with a C. D. of 50 amperes per square foot it was: At 20° C. = 1.19 V., at 40° C. = 0.88 V., and at 60° C. = 0.78 V.

The average e.m.f. of the fluo-silicate cells, with a C. D. of 10 amperes per square foot was: At 20° C. = 0.22 V., at 40° C. = 0.15 V., at 60° C. = 0.10 V.; with a C. D. of 50 amperes per square foot it was: At 20° C. = 0.84 V., at 40° C. = 0.58 V., and at 60° C. = 0.49 V.

The average e.m.f. of the chloride cells, with a C. D. of 10 amperes per square foot was: At 20° C. = 0.45 V., at 40° C. = 0.20 V., at 60° C. = 0.14 V.; with a C. D. of 38 amperes per square foot it was: At 40° C. = 0.88 V., at 50° C. = 0.68 V., and at 60° C. = 0.38 V.

The results of these sets of experiments may be summarized as follows: The deposits formed in copper sulphate electrolytes at 40° C. were smoother and brighter than those formed at a temperature of 20° or 60° C.; however, in the case of the fluo-silicate electrolytes, the smoother and the brighter deposits formed at 60° C.; and, also, the deposits formed in the fluo-silicate electrolytes were much brighter and less crystalline than those formed in sulphate electrolytes, the conditions of electrolysis being the same.

The deposits which formed in the cuprous chloride electrolytes were, in each case, very satisfactory, being precipitated as loosely-adherent, spangular, plate-crystals, which, unless the electrolytes were most vigorously stirred, would have bridged the electrodes and short-circuited them. Variation of the temperature of the electrolytes, and of the current density, caused no apparent improvement on the deposition.

III. Silver Electrolytes, Which Contained no Addition-Agent.

The electrolyses of the silver electrolytes were conducted with solutions of silver nitrate, and silver fluo-silicate, which contained 4 grams of silver per 100 c.c. solution.

The silver nitrate solution was prepared by dissolving a weighed amount of pure, electrolytic silver in nitric acid, evaporating to dryness, taking up with distilled water, adding a few drops of nitric acid, and finally diluting to such a volume that it contained 4 grams of silver per 100 c.c. solution.

The silver fluo-silicate electrolyte contained 4 grams silver and 0.67 gram free fluo-sicilic acid per 100 c.c. solution (or a quarter molecular equivalent of free acid). It was prepared as outlined under the heading *Preparation of Electrolytes.*

The anodes were sheets of rolled silver, about one-sixteenth inch thick, and the cathodes were thin, polished sheets of silver. The surface of the electrodes exposed to electrolytic action was 2 by 2.25 inches, or 4.5 square inches. The distance between the anode and the cathode of each cell was one inch; they were held in place by a wooden spanner, similar to those used for the lead, and copper electrodes.

In order to determine the effect of temperature upon the character of the deposit, the experiments were conducted with a set of three cells connected in series; the temperature of one cell was maintained at 20° C., one at 40° C., and one at 60° C., by having the cells in separate water-baths.

The current density used was 15 amperes per square foot. The average e.m.f. of the nitrate cells was: At 20° C. = 0.88 V., at 40° C. = 0.62 V., and at 60° C. = 0.51 V.; that of the fluo-silicate cells was: At 20° C. = 0.71 V., at 40° C. = 0.50 V., and at 60° C. = 0.41 V.

The deposits formed at 40° C. in the nitrate, and in the fluo-silicate, electrolytes were more coherent, and the crystals, of which the deposits were composed, were of less length than those formed in the electrolytes at 20° C. and at 60° C. The deposits formed in the electrolytes at 60° C. were not so coherent as those formed in the electrolytes at 20° C. or at 40° C.

The deposits formed in fluo-silicate electrolytes were more

coherent than those formed in the nitrate electrolytes, when the temperature and the current density in each case were the same.

During the electrolysis of the fluo-silicate electrolytes, a small amount of flocculent silica separated, and for the most part remained suspended in the solution, but did not interfere with the electrolysis.

IV. Lead Electrolytes, Which Contained Addition-Agent.

This series of experiments was conducted with lead electrolytes, to which were added a small amount of an addition-agent.

The size of the electrodes, their distance apart, and the volume of the electrolytes were the same as operated with, when no addition-agent was present (Series I.).

As it was found that free acid in the lead nitrate electrolytes (Series I.) caused chemical corrosion of the electrodes, the free acid in the nitrate electrolytes of this series was reduced to 0.75 gram per 100 c.c. solution (one-eighth molecular equivalent of free acid).

The lead fluo-silicate electrolytes were of similar percentage composition to those used in Series I.

The current density used was 30 amperes per square foot, and the temperature of the electrolytes 20° C., these conditions having been selected because of the fact that deposits of lead formed with higher current density and at lower temperatures are more crystalline and less coherent; therefore, by electrolyzing under these conditions, the effect of the presence of an addition-agent could be more readily distinguished.

The addition-agents tried were tannin, resorcinol, pyrogallol, and gelatine, each of which was dissolved in a quantity of warm distilled water, diluted to a measured volume and added to the respective electrolytes in measured amounts. The volume of the solution added at the start was such that the electrolyte contained one part by weight of the addition-agent in 5,000 parts of electrolyte. When it was found that the character of the deposition was not altered, a further addition was made. In the cases of the lead nitrate electrolytes, it was found that these addition-agents restrained the crystallization to a certain extent, when they were present in the proportion of about one part by weight to 250 parts of electrolyte; but even when present in this large

proportion, the deposition was unsatisfactory, especially with each of the addition-agents except tannin. With tannin, the deposit was much better than those formed in the electrolytes which contained one of the other addition-agents. The presence of the tannin, in the lead nitrate electrolyte, caused the precipitation of the metal as a more coherent, less sharply crystalline mass; instead of the crystals forming with sharp edges, they verged into the nodular condition.

With the lead fluo-silicate electrolytes, it was found that when either tannin, pyrogallol, or gelatine are present in the proportion of one part by weight in 5,000 parts of the electrolyte, the lead deposited as a bright, solid, coherent mass, whereas, when the addition-agent was absent, the deposit forms as a mass of non-coherent, dendritic crystals. The most satisfactory of these three addition-agents was found to be gelatine, which caused the lead to deposit smooth, bright, dense, and free from apparent crystallization. Tannin had the same effect as the gelatine, but to a slightly less degree; it caused the lead to deposit smooth, bright and dense, but with an apparent crystalline structure. Pyrogallol was not so effective as the tannin; with the presence of one part in 5,000 parts of electrolyte, the lead deposited as a dense, coherent mass, with adherent dendrites along the edge of the cathode. Possibly by increasing the proportionate amount of the pyrogallol, the deposit will form free of the dendrites. Resorcinol was found to be an unsatisfactory addition-agent for lead fluo-silicate electrolytes, even when present in the proportion of one part in about 1,000 parts; it restrained the crystallization of the deposition, but did not cause it to form as a dense, coherent mass.

The average e.m.f of the nitrate cells was 0.44 V., with a C. D. of 30 amperes per square foot, and the temperature of the electrolyte at 20° C.; the average e.m.f of the fluo-silicate cells was 0.58 V. with same C. D. and temperature. Time of run was 185 minutes.

V. Copper Electrolytes, Which Contained Addition-Agent.

This series of experiments was conducted with copper electrolytes, to which were added one of the addition-agents.

The composition of the electrolytes were the same as those which were used in the experiments of Series II. The temperature of the electrolytes in one set of experiments was approximately 30° C.; and in the other set it was 20° C. The current density in each case was maintained at about 50 amperes per square foot.

The addition-agents tried with the copper sulphate electrolytes were tannin, resorcinol, pyrogallol, and gelatine; those tried with the copper fluo-silicate electrolytes were tannin, pyrogallol, and gelatine; and those with the cuprous chloride electrolytes were pyrogallol, gelatine, and dextrine.

Standard solutions of the addition-agents were prepared by dissolving a weighed amount of each in warm water and diluting the solution to a measured volume. A certain measured volume of each of these standard solutions was added to the respective electrolytes, and the effect of its presence noted. The first amount added was of such a volume as to give an electrolyte containing one part of reagent per 5,000 parts of solution. If no apparent effect was noted at once, a further addition of the standard solution was made, and this repeated until an alteration in appearance of the deposition was apparent.

With the copper sulphate electrolyte it was found that the presence of either tannin or resorcinol in the proportion of one part per 2,500 parts of electrolyte, or of gelatine in the proportion of one part per 800 parts of electrolyte caused the copper to deposit bright and smooth. The deposits were rendered more smooth by maintaining the temperature at 30° C., than at 20° C. Pyrogallol in the proportion of 1 part in 5,000 parts of electrolyte did not improve the deposition, but caused it to form darker; increased amounts caused the deposit to form much darker.

The deposits from the copper fluo-silicate electrolytes were rendered more smooth and brighter by the presence of a small amount of either tannin (1 part: 5,000), pyrogallol (1 part: 1,000), or gelatine (1 part: 5,000). Tannin was the most effective addition-agent, and pyrogallol and gelatine somewhat less effective, but similar to each other. By electrolyzing at 30° C., instead of at 20° C., the deposits formed smoother and brighter.

The presence of either pyrogallol, gelatine or dextrine in the

cuprous chloride electrolytes in varying proportions from 1 : 5,000 up to 1 : 500 did not restrain the crystallization of the deposited copper. These experiments were repeated several times, but as they gave no promise of success in producing solid, coherent deposits, the cuprous chloride electrolyte was not further tried.

The average e.m.f. of the sulphate cells, with the electrolytes at 20° C., and C. D. of 50 amperes per square foot, was 1.64 V.; and with the electrolytes at 31° C., it was 1.42 V.

The average e.m.f. of the sulphate cells, with the electrolytes at 20° C., and C. D. of 50 amperes per square foot was 1.10 V.; and at 30° C., it was 0.97 V.

The average e.m.f. of the chloride cells, with a C. D. of 40 amperes per square foot, and temperature of 20° C., was 1.45 V.

VI. Silver Electrolytes, Which Contained Addition-Agents.

The effect of the presence of addition-agent was determined by electrolyzing solutions of similar composition to those used for Series III.

The addition-agents tried were tannin, resorcinol, pyrogallol, and gelatine. Standard solutions of these were made in the same manner as previously described, and a measured volume added to the respective electrolytes.

The current density employed was 16 amperes per square foot, and the temperature of the electrolytes was 20° C.

The only favorable results obtained by this series of runs were those with the electrolytes which contained gelatine in the proportion of one part by weight to 14,000 parts of electrolyte. The presence of the gelatine restrained the crystallization of the deposition, causing the crystals to form smaller, and to adhere more firmly to the cathode. A further increase of gelatine was made, gradually increasing the proportionate amount to one part in 3,500 parts of electrolyte, but no improvement in the deposition was noted; in fact, with the greater amount present, the deposition was less satisfactory.

On adding one part pyrogallol to 10,000 parts of the silver solutions, a dark, slimy precipitate of cement silver was produced, and the cathode deposit formed as black, non-adherent precipitate.

Resorcinol in the proportion of one part per 1,700 parts of

electrolyte and tannin in the proportion of one part per 11,000 parts had no beneficial effect upon the deposits of silver formed in the silver nitrate electrolytes, but the effect of their presence in the silver fluo-silicate electrolytes was apparent. With the tannin in the latter electrolyte, in the proportion of one part by weight to 11,300 parts of electrolyte, the deposit was darkened, and the crystals composing the deposit were smaller and more coherent than when no tannin was present. The presence of resorcinol in the silver fluo-silicate electrolyte, in the proportion of one part by weight to 1,700 parts of electrolyte, slightly improved the coherency of the deposit.

The effect of the presence of any one of the four addition-agents, in larger amounts than these proportions was found to be detrimental instead of beneficial. The amounts in each case were increased to one part in about 2,500 parts of electrolyte, and without an exception, no improvement on the deposition of the silver resulted; the effect of the larger amount was a less adherent deposit, a darker colored electrolyte, and the precipitation of colloidal silver.

The electrolytes to which any one of the four addition-agents was added, even in the smallest amount, became dark colored on standing.

The e.m.f. of the nitrate cells averaged 0.88 V., and that of the fluo-silicate cells averaged 0.82 V., when the C. D. in each case was 16 amperes per square foot and the temperature of the electrolytes was about 20° C.

EXPERIMENTAL: PART II.[25]

The salts which were selected for the preparation of nickel electrolytes to be investigated, were: nickel fluo-silicate, nickel chloride, nickel sulphate and nickel fluo-borate, because of their higher solubility and their cheapness of preparation.

The chloride and the sulphate solutions were prepared by dissolving a weighed amount of the salts in water, adding the calculated amount of acid and diluting to the required volume. The fluo-silicate was prepared by adding a calculated amount of C.P. nickel oxide (black) to a measured volume of 39.5 per cent H_2SiF_6 and heating to about 45° C., which gave a clear, blue solution. A small amount of silica separated, it was filtered off,

[25] School of Mines Quarterly, **29**, 342-370, Kern and Fabian; Kern and Frapwell.

and the clear solution analyzed for nickel and H_2SiF_6. It was then diluted so as to contain 8 grams of nickel and the calculated amount of free H_2SiF_6 per 100 c.c.

I. Nickel Electrolytes, Which Contained a Half Molecular Equivalent of Free Acid.

This set of experiments was made with three sets of three cells each, connected in series. Each set consisted of a chloride, a sulphate and a fluo-silicate cell. One set was electrolyzed at 18° to 20° C., the second set at 38° to 41° C., and the third set at 57° to 62° C. The second and the third sets were heated in water-baths.

All of the electrolytes contained 8 per cent. nickel and a half molecular equivalent of free acid. They were electrolyzed with cast nickel anodes (containing 92 per cent. nickel, 5 per cent. iron, carbon), and thin sheet nickel cathodes, size of each 2½ inches by 2¼ inches (5.6 square inches surface exposed), placed one inch apart.

During the electrolysis, gasing occurred at all of the cathodes, but apparently none at the anodes. There was less gasing in the cells at the higher temperatures than in those operated at ordinary temperature. A small amount of gelatinous silica separated in the fluo-silicate electrolytes collecting in the bottom of the cell and on the electrodes, more so on the cathode which was at 18° to 20° C., than on those which were in the heated electrolytes.

The electrodes were weighed before and after the run, and the anode and cathode current efficiency calculated. The electrolysis was conducted at a current density of 10 amperes per square foot, and at e.m.f. as recorded in Table I. The electrochemical equivalent of nickel was taken as 1.095 grams per ampere-hour, which factor was used for calculating the current efficiencies. The theoretical amount of nickel deposited in three hours by 0.39 amperes is 1.281 grams.

II. Nickel Electrolytes, Which Contained a Tenth Molecular Equivalent of Free Acid.

The results of the above experiments showed that the presence of a large amount of free acid in the electrolyte caused very low current efficiencies, as well as the formation of unsatisfactory

deposits, so it was decided to reduce the free acid to one-tenth (or 10 per cent.) the molecular equivalent of the salt in solution, still maintaining the nickel at 8 grams per 100 c.c. The chloride electrolytes contained 32.40 grams $NiCl_2.6H_2O$, and 2.2 c.c conc. HCl (sp. gr. 1.20) or 1.0 grams free HCl, per 100 c.c The sulphate electrolytes contained 38.25 grams $NiSO_4.7H_2O$ and 0.70 c.c. conc. H_2SO_4 (sp. gr. 1.84), or 1.34 grams free H_2SO_4 per 100 c.c. The fluo-silicate electrolytes contained 42.12 grams $NiSiF_6.6H_2O$ and 1.96 grams H_2SiF_6 per 100 c.c.

The runs were made by electrolyzing a cell of each at 20° C., 40° C. and 60° C., with a current density of 10 amperes per square foot, using cast nickel anodes (containing 92 per cent. Ni and 5 per cent. Fe) and sheet nickel cathodes, size 2½ by 2¼ inches, held one inch apart.

The cathode efficiencies in the chloride electrolytes were quite an increase, showing that neutral solutions should be employed. The great difference in the cathode efficiencies also indicates that sulphuric acid is a stronger acid than either hydro-fluo-silicic or hydrochloric acid; that is, it is ionized to a much greater degree than the other two acids, and is a better conductor of the current than the nickel salt.

The data of these runs are recorded in Table I.

III. Nickel Electrolytes, Which Were Neutral.

As the presence of free acid in the electrolytes prevented the satisfactory deposition of nickel, and also caused low current efficiencies, the next runs were made with neutral solutions.

The electrolytes were prepared by dissolving a weighed amount of the air-dried salts in water and diluting to a volume that contained 8 grams nickel per 100 c.c.

The nickel fluo-silicate salt was prepared by slowly evaporating the solutions in a water-bath, and collecting the crystals, which were washed and dried. A precaution in preparing this salt is to evaporate the solution at a temperature below 75° C., as at higher temperatures the salt is decomposed; quite rapidly at boiling.

As the composition of the fluo-silicate salt was questioned, an air-dried sample was taken and analyzed. Its composition was found to be $NiSiF_6.6H_2O$.

With the exception that the electrolytes were neutral, the conditions of these were the same as those of Experiments I and II.

In order to measure the exact amount of current which passed, and to get the efficiency more correctly, a standard copper coulomb-meter was placed in the circuit. This consisted of two sheet copper electrodes in an electrolyte containing 15 grams copper sulphate crystals, 5 c.c. conc. H_2SO_4, and 5 c.c. ethyl alcohol per 100 c.c. solution. From this electrolyte, one ampere flowing per minute deposits 0.01976 gram copper, or one ampere-hour deposits 1.1856 grams copper. One ampere-hour theoretically deposits 1.0950 grams nickel.

During the electrolysis there was scarcely any gasing at the electrodes in the chloride electrolytes, and extremely little in the other electrolytes, however, more in the sulphate electrolytes than in the fluo-silicates. In the sulphate electrolytes the gasing seemed to increase as the electrolysis progressed, and also the e.m.f. increased, whereas the e.m.f. of the chloride and the fluo-silicate cells decreased. The results are recorded in Table I.

The apparently very high current efficiencies of the three sulphate electrolytes was due to basic salts which separated during the electrolysis and gathered in crevices, the result of splitting of the deposits. The basic sulphate salts, being insoluble in water, could not be removed by washing. There was also considerable separated from the solution and collected in the bottom of the cell.

The deposits from the chloride and the fluo-silicate electrolytes were very satisfactory. The deposits from the chloride electrolytes were of a dull white to light olive-gray color, finely crystalline and coherent, but showed a slight tendency to peel from the cathode in the cold solutions, whereas in the heated solutions the deposits did not crack or peel, and also were fairly flexible. The deposits from all the fluo-silicate electrolytes were bright, non-crystalline, tough, flexible and adherent, and in no case showed any tendency to crack.

During electrolysis a small amount of gelatinous silica separated in the fluo-silicate electrolytes, and settled to the bottom of the cells, more in the one which was heated to 60° C. than in the others. The solutions remained clear.

Some basic salts formed in the chloride electrolytes, but did not

interfere with the deposition, as there was such a small amount. On addition of a few drops of acid the solution became clear.

The impurities in the nickel remained as black finely divided sludge which adhered and retained the original shape of the anodes.

IV. Nickel Electrolytes, Which Contained No Free Acid.

These runs were conducted with a current density of about 20 amperes per square foot, the nine cells and the copper coulometer being arranged in series; two sets of the cells were heated in a water-bath at 40° and 60° C. similar to the previous runs. The anodes were cleaned of adhering sludge, and a new set of cathodes used. The electrolytes were neutral solutions containing 8 per cent. nickel, the same ones which were used for previous runs.

The electrolysis was conducted for eight hours with a current of 0.8 ampere (20 amperes per square foot of electrode surface).

The results are given in Table I.

Table I.

Composition of the Electrolytes	Experiment	Temperature °C.	C. D. Amperes per sq. ft.	Time of Run Minutes	$NiCl_2$ Electrolyte		$NiSO_4$ Electrolyte		$NiSiF_6$ Electrolyte	
					Average e.m.f. Volts	Cathode Current Efficiency Per cent.	Average e.m.f. Volts	Cathode Current Efficiency Per cent.	Average e.m.f. Volts	Cathode Current Efficiency Per cent.
8% nickel and half molecular equivalent of free acid.	I.	20	10	180	0.49	3.20	0 89	0 86	0.96	0.78
		40	10	180	0.36	1.25	0.65	0.62	0.78	1.64
		60	10	180	0 21	1.01	0.42	0.39	0.61	1.80.
8% nickel and $\frac{1}{10}$ the molecular equivalent of free acid.	II.	20	10	255	0.73	62.6	0.91	1.50	0.82	2.20
		40	10	255	0.52	79.0	0.78	1.60	0.83	4.90
		60	10	255	0.35	71 0	0.51	1.50	0.61	4.80
Neutral solutions containing 8% nickel.	III.	20	10	255	0.78	96.6	1.50	102.2	1.05	92.1
		40	10	255	0 59	99.4	1.35	106.9	0.94	92.4
		60	10	255	0.44	99.2	0.88	101.1	0.73	89.8
Neutral solutions containing 8% nickel.	IV.	20	20	480	1.06	91.2	3.45	. . .	1.45	96.8
		40	20	480	0 73	94.7	2.30	. . .	1.24	100.0
		60	20	480	0.64	88.3	1.40	. . .	1.01	90.3
Neutral solutions containing 8% nickel and a half molecular equivalent of sodium salt	V.	20	20	180	1.02	90.2	3.12	10.2	. . .	. . .
		60	20	180	0.58	99.7	0.96	99.8	. . .	. . .

In the three sulphate cells there was considerable gasing at the cathodes, and the separation of a yellow basic salt, which collected on the electrodes and floated in the solution. The deposit formed as a black, spongy, non-adherent mass intermixed with basic salts, so these cells were cut out of the circuit after an hour and three quarters.

The only gasing noticed in the chloride and the fluo-silicate electrolytes was a very slight amount, when the current was first started, but after a few minutes this ceased.

As the electrolysis continued, a small amount of basic salts formed in the chloride cells, but this floated and did not interfere with the deposits. The deposits in these cells were very satisfactory, forming as solid finely crystalline sheets, which were fairly flexible. The deposit formed at 20° C. towards the end of the run, cracked from the edge of the cathode and bent towards the anode, whereas the deposits formed at 40° and at 60° C. showed no tendency to peel. The deposit from the solution at 20° C. was darker than those from the solutions at 40° and 60° C. The brightest deposit from the chloride electrolytes formed in the hottest solution.

The deposits from the three fluo-silicate electrolytes were perfect, being bright, very smooth, flexible and adherent, showing no tendency to peel. The electrolyte underwent slight decomposition, causing the precipitation of gelatinous silica, which floated in the solution and settled to the bottom of the cells. The greater amount formed in the cell which was heated at about 60° C. The solutions, however, remained very clear, no basic salts formed.

The impurities in the nickel remained as black sludge, retaining the original shape of the anodes.

V. Nickel Electrolytes, Which Contained Sodium Salts.

These runs were made in order to see if the addition of sodium salts to the chloride and the sulphate solutions would be beneficial. They were added in one half (or 50 per cent.) the molecular proportion of the nickel salts present (as $NiX_2 + NaX$). The chloride solution contained 32.40 grams $NiCl_2.6H_2O$, and 8.0 grams NaCl per 100 c.c., or 8 per cent, nickel and 3.15 per

cent. sodium. The sulphate solution contained 38.25 grams $NiSO_4.7H_2O$ and 21.94 grams $Na_2SO_4.10H_2O$ per 100 c.c., or 8 per cent. nickel and 3.14 per cent. sodium. These solutions were electrolyzed at 20° C. and at 60° C., in the same manner as the previous runs, using the same sort of electrodes, and with a current density of 20 amperes per square foot (0.8 ampere).

The results are given in Table I.

The addition of sodium salt to the sulphate electrolyte had the effect of increasing the conductivity, especially when the electrolysis was conducted at 60° C. The deposit from the heated sulphate electrolyte was very satisfactory; it was a smooth, solid, adherent, dull-white deposit free from cracks, and the current efficiency of this deposition approximated 100 per cent. The deposit from the sulphate electrolyte at 20° C. was dark, but solid, and was attached to the plate as a number of small curls. The efficiency of the deposition from the sulphate electrolyte at 20° C. was quite low, due to considerable gasing at the electrodes, as the result of high e.m.f., whereas the e.m.f. of the sulphate electrolyte, which was at 60° C., was below 1.1 volts.

Comparing the e.m.f. of the chloride electrolytes with the e.m.f. of the electrolytes which contained no sodium chloride (Experiment IV), it is seen that the conductivity is not altered much by the presence of the sodium salt, but its presence is beneficial in that the current efficiency is increased in the heated electrolyte.

The average data of these runs are given in Table I.

Electrolysis of Nickel Fluo-silicate and Nickel Fluoborate Electrolytes.

Nickel Fluo-silicate Electrolyte.

The deposits of nickel from neutral nickel fluo-silicate electrolytes were so very satisfactory in the previous runs, when the electrolysis was continued for three to five hours, that a run for about 115 hours was made in order to see what effect time had upon the character of the deposit. The electrolysis was conducted with a current density averaging 15 amperes per square foot at an e.m.f. of 1.10 to 1.18 volts, and temperature of electrolyte from 40° to 55° C.

The electrolyte was a neutral solution of nickel fluo-silicate,

containing about 7 per cent. of nickel. The electrodes were two cast anodes, containing 92 per cent. nickel, 5 per cent. iron, carbon and trace of copper, size 3 inches by 4 inches, between which was placed a sheet nickel cathode, size 3½ inches by 4 inches. The space between the electrodes was about ¾ inch.

During electrolysis, some gelatinous silica separated from the electrolyte, but did not interfere with the deposition, as it settled to the bottom of the cell. The solution remained clear.

The corrosion of the anodes was very even, the impurities (C, Fe, and Cu) remained as adherent sludge, which retained the original form of the anodes.

The deposit was bright, perfectly smooth, flexible and free from apparent crystallization. It formed $\frac{3}{16}$ inch thick and weighed 214 grams.

Nickel Fluo-borate Electrolyte.

Very satisfactory deposits of nickel were also produced in nickel fluo-borate electrolytes, which were prepared by adding a calculated amount of boric acid crystals to a 40 per cent. solution of hydro-fluoric acid. The reaction is shown by the equation:

$$H_3BO_3 + 4HF = HBF_4 + 3H_2O.$$

The neutral nickel solution was prepared from this by adding nickel carbonate until the acid was completely neutralized:

$$2HBF_4 + NiCO_3 = Ni(BF_4)_2 + H_2O + CO_2.$$

The clear blue solution was diluted so as to contain 8 per cent. nickel, and electrolyzed at room temperature, in glass beakers. The electrodes were two cast nickel anodes containing 92 per cent. Ni and 5 per cent. Fe, size 2¾ inches by 2¼ inches, between which was placed a sheet nickel cathode of same size. The space between the electrodes was about ¾ inch.

The electrolysis was continued for about 300 hours with a current density averaging 12 amperes per square foot, and an e.m.f. of 1.10 to 1.25 volts.

The deposit formed $\frac{5}{16}$ inch thick and weighed 290 grams. It was a perfectly satisfactory deposit, being bright, smooth, malleable, solid and adherent, differing from the fluo-silicate deposits in that it was not quite so smooth, but was more nodular, especially on the edges.

Several preliminary runs were made by electrolyzing at 40° C. and at 60° C., but were unsatisfactory, as the solutions decomposed, resulting in the precipitation of a light green insoluble salt. At temperatures below 30° C., this salt did not form, and the solution remained clear during the electrolysis, and on standing for several months. The solution was kept in glass bottles for over fifteen months, during which time the glass was not corroded.

Transparent light green crystals of nickel fluo-borate were obtained by slowly evaporating the solution at temperatures not exceeding 35° C. At higher temperatures, the solution decomposes with the separation of a light green insoluble salt.

EXPERIMENTAL: PART III.[26]

Ferrous Sulphate and Ferrous Chloride Electrolytes.

The sulphate and chloride solutions used for the preliminary experiments were prepared by dissolving the salts in water, and diluting to such a volume that they contained the desired per centage of constituents (which was decided by the solubility of the salts).

Electrolytes used for a later set of experiments were prepared by taking a calculated amount of dilute acid (HCl or H_2SO_4) and neutralizing with iron, in the form of an iron-graphite couple, similar to an electric cell.

(*a*) The ferrous sulphate solution contained 40 grams $FeSO_4$ $7H_2O$ per 100 c.c., giving an electrolyte containing about 8 per cent. of iron (8 grams Fe per 100 c.c).

(*b*) The ferrous-sodium sulphate solution contained 30 grams $FeSO_4$ $.7H_2O$, and 21 grams Na_2SO_4 $.10H_2O$ (Glaubers' Salt) per 100 c.c., giving a solution containing about 6 per cent. of iron and 3 per cent. of sodium.

(*c*) The ferrous-sodium chloride solution contained 28.5 grams $FeCl_2$ $.4H_2O$, and 10.2 grams NaCl per 100 c.c., giving an electrolyte containing 8 per cent. of iron and 4 per cent. of sodium.

The electrolysis were conducted in glass beakers holding about 650 c.c. of the electrolyte, using one anode and one cathode. Distance between the electrodes was 1.25 inch.

[26] Transactions of Am. Elect. Chem. Soc. **13**, (1908); 103-125.

The anodes and the cathodes were strips of sheet wrought iron, which were well cleaned of all rust and scale. The cathodes were lightly coated with vaseline and wiped with a clean rag, leaving just sufficient grease to allow the deposit being stripped. The surface exposed of each electrode was 3 inches by 3.5 inches, or 10.5 square inches.

The temperature of the electrolytes was maintained uniform by placing the cells on a hot plate.

The results of the runs are tabulated in Table II.

The addition of a few drops of acid to the electrolytes was made each day for the purpose of dissolving the basic salts, which was the result of atmospheric oxidation of the neutral electrolytes. When the acid was added, the turbid solutions became clear and gasing at the cathodes continued until the free acid was neutralized.

TABLE II.

Composition of the Electrolytes	Experiment No.	Average C. D. per sq. ft.	Average e.m.f. of cell	Temperature of Electrolyte °C.	Time of Run Hours	Weight of Deposit grams	Current Efficiency	Character of the Deposit
8% iron as sulphate . .	1	14	0.89 v.	47° to 55°	44	44.62	97.51%	Smooth crystalline deposit.
6% iron and 3% sodium as sulphates	2	14	0.58 v.	47° to 55°	44	44.98	98.3%	Smooth deposit, less crystalline than No. 1.
8% iron and 4% sodium as chlorides	3	14	0.48 v.	47° to 55°	44	45.26	98.9%	Smooth deposit, no apparent crystallization.
8% iron and 4% sodium as chlorides	4	15	0.47 v.	44° to 50°	77	83.98	93.5%	Smooth deposit, no apparent crystallization.
8% iron and 4% sodium as chlorides	5	15	0.49 v.	46° to 53°	77	84.15	93.7%	Smooth deposit, no apparent crystallization.
8% iron and 4% sodium as chlorides	6	15	0.48 v.	42° to 47°	77	83.87	93.4%	Smooth deposit, no apparent crystallization.
8% iron and 4% sodium as chlorides	7	15	0.47 v.	45° to 67°	385	939.30	93 +%	Nodular deposit, no apparent crystallization.
8% iron and 7% sodium as chlorides	8	15	0.45 v.	44° to 63°	450	1135 50	92.+%	Non-crystalline, and fairly smooth.

Before starting to take the records, the solutions were first boiled, then electrolyzed for about three hours, using wrought iron anodes and cathodes, in order to reduce any ferric salts present and to get the electrolytes in proper working condition. At the start there was considerable gasing at the cathodes, and the deposits split and curled; but after about two hours' running, the deposits began to form smoothly and to adhere.

When the electrolytes were found to be in good condition, the anodes and cathodes were replaced by the weighed anodes and cathodes, and the records were taken as tabulated in Table II.

Deposits No. 1 and No. 2 were more brittle than those formed in the chloride electrolytes; they had the appearance on their surface of being made up of a solid mass of minute rhombic crystals; whereas, deposits from the chloride electrolytes had no apparent crystalline form, but was perfectly smooth with numbers of scattered small protruding nodules, especially along the edges. These deposits were also more flexible than those which were formed in the two sulphate electrolytes.

The deposit from cell No. 8, which contained an electrolyte composed of 8 per cent. iron and 7 per cent. sodium as chlorides, was non-crystalline, very dense and fairly smooth. It was less nodular and less vertically ridged than the deposits formed in the electrolytes which contained 4 per cent. sodium (cells No. 3 to No 7). The presence of the larger amount of sodium chloride in the electrolyte retarded the formation of nodules, and also prevented the vertical ridging of the deposit.

Summary of Experimental Part.

The deposits of lead, copper, and silver tend to form more crystalline and less coherent with higher current densities. The smoother deposits form with lower current densities.

With rise in temperature, of the electrolytes of lead, copper, and silver, up to 60° C., the tendency of the depositions is to form more coherent, denser, and less crystalline.

The fluo-silicate electrolytes of lead, copper, and silver give more coherent deposits than those formed in the nitrate electrolytes of lead or silver, or in the sulphate or chloride electrolytes of copper.

The crystallization of the deposits of lead, formed in an almost

neutral electrolyte of lead nitrate, is restrained by having present one part of either tannin, resorcinol, pyrogallol or gelatine per 250 parts of electrolyte. The deposits, however, in all cases were composed of a mass of non-coherent crystals. Tannin is the most satisfactory "addition-agent" for lead nitrate electrolyte.

Gelatine, tannin, and pyrogallol, when present in lead fluo-silicate electrolyte in the proportion of one part by weight to 5,000 parts electrolyte causes the lead to deposit as a smooth, dense, coherent mass. The most effective of these "addition-agents" is gelatine, the next is tannin, and the least effective is pyrogallol. Resorcinol is not a suitable "addition-agent" for this electrolyte.

The deposits of copper, from copper sulphate electrolytes, are rendered smoother and brighter by the presence in the electrolyte of either tannin, resorcinol or gelatine; tannin is the most effective, resorcinol is less, and gelatine is the least effective of the three. Pyrogallol is not a suitable "addition--agent" for this electrolyte, as it causes the deposited copper to form dark colored.

The deposits of copper from copper fluo-silicate electrolyte were rendered smoother and brighter by the presence in the electrolyte of either tannin, pyrogallol or gelatine. Tannin is the most effective of the three.

The deposits of copper from cuprous chloride electrolytes are not improved by the presence in the electrolyte of either gelatine, pyrogallol or dextrine. Elevation in temperature of this electrolyte does not cause the copper to deposit more coherent.

Silver is deposited as finer crystals and in a more coherent form from electrolytes of silver nitrate and silver fluo-silicate, when the electrolytes are at a temperature of 40° C., than when at a temperature of either 20° or 60° C.

Deposits of silver from silver fluo-silicate electrolyte are more coherent than deposits formed in silver nitrate electrolyte.

Gelatine, when present in silver nitrate, and in silver fluo-silicate, electrolytes, in the proportion of one part per 10,000 to 14,000 parts electrolyte, causes the deposit to form as shorter, and as smaller crystals, which are more coherent than when gelatine is not present.

Pyrogallol, tannin and resorcinol are not suitable "addition-agents" for silver nitrate, or fluo-silicate electrolytes.

Table III.

Effect of Organic Addition-agents in the Electrolytes of Lead, Copper and Silver.

Electrolyte	Gelatine	Tannin	Pyrogallol	Resorcinol
$PbSiF_6$	Densest deposit.	Denser deposit.	Dense deposit.	Deposit not improved.
$CuSiF_6$	More smooth and bright deposit.	Most smooth and bright deposit.	Smooth, dense deposit.	Deposit not improved.
Ag_2SiF_6	Coherent deposit.	Deposit not improved.	Deposit not improved.	Deposit not improved.
$Pb(NO_3)_2$.....	Less crystalline and more coherent deposit.	Deposit much improved.	Deposit not improved.	Deposit not improved.
$AgNO_3$	More coherent deposit.	Deposit not improved	Deposit not improved.	Deposit not improved.
$CuSO_4$	Brighter and smoother deposit.	Brighter and smoother deposit.	Dark deposit.	Deposit not improved.
$Cu_2Cl_2.xNaCl$	Deposit not improved.	Deposit not improved.	Deposit not improved.	Deposit not improved.

The presence of free acid in nickel chloride, nickel sulphate and nickel fluo-silicate electrolytes caused very low cathode efficiency, whereas the anode efficiency was in most cases over 95 per cent. By continued electrolysis the free acid was neutralized and the cathode efficiency increased.

The electrolysis of neutral nickel chloride and nickel fluo-silicate solutions with current densities of 10 and 20 amperes per square foot gave very satisfactoy deposits, and high current efficiencies. Neutral nickel sulphate solutions were unsatisfactory, as precipitates of insoluble basic salts formed and intermixed with the deposited nickel.

Heating the nickel chloride and the nickel fluo-silicate electrolytes decreased the e.m.f., increased the current efficiencies, and improved the deposition. The most satisfactory temperature was about 40° C.

During electrolysis of nickel fluo-silicate solutions, a small amount of gelatinous silica separated, and collected on the bottom of the cells. Heating of these solutions above 75° C. also caused the separation of silica, but very slowly.

A small amount of basic salts separated from the neutral nickel chloride electrolytes during electrolysis, but did not interfere with the deposition. The presence of a small amount of free acid prevented their formation.

The presence of sodium salt in the nickel chloride electrolytes was not very beneficial, whereas its presence in the neutral sulphate electrolytes reduced the e.m.f. over 60 per cent., caused the formation of good deposits and also increased the current efficiency to approximate 100 per cent. when the temperature of the electrolyte was about 60° C. At room temperature the presence of the sodium salt in the sulphate electrolyte was of no great benefit.

Satisfactory deposits of nickel were obtained from neutral solutions of nickel fluo-borate electrolytes, when the electrolysis was conducted at room temperature, and using a current density of 10 to 15 amperes per square foot. At temperatures above 35° C. the solution was decomposed, causing the precipitation of an insoluble basic salt.

Good deposits of iron were obtained by the electrolysis of neutral electrolytes containing either 8 per cent. of iron as $FeSO_4$, or 6 per cent. Fe and 3 per cent. Na as sulphates, or 8 per cent. Fe and 4 to 7 per cent. Na as chlorides. The presence of the larger amount of sodium chloride in the electrolytes prevented the vertical ridging of the deposit, and caused it to form smoother. The finer grained deposits of iron from the sulphate electrolytes were formed in the solutions which contained the sodium salt.

The deposits of iron formed in neutral chloride electrolytes containing sodium chloride were finer grained and more flexible than those formed in neutral sulphate electrolytes.

The deposits of iron formed smoother when the electrolysis was conducted at 40 to 60° C. than when conducted at normal temperature.

Conclusions.

The effect which the presence of organic addition-agents has upon the deposits of lead and silver from their fluo-silicate and their nitrate electrolytes, and upon the deposits of copper from its fluo-silicate and its sulphate electrolytes, cannot be attributed to any specific physical property of the addition-agent.

The only property in common of the organic addition-agents which were found to be beneficial in improving the deposits of lead, copper and silver, is the larger number, and the similar

arrangement of the hydroxyl radicals. The hydroxyl radicals of pyrogallol and of tannin are in the position 1, 2, 3, in the benzene ring. Resorcinol ($C_6H_4(OH)_2$) differs from pyrogallol ($C_6H_3(OH)_3$) in that it contains two hydroxyls in the position 1, 3. Therefore, to the extra hydroxyl of pyrogallol, in the position 2, may be attributed the cause of rendering denser, smoother and brighter deposits from lead fluo-silicate and copper fluo-silicate electrolytes.

Tannin ($C_{12}H_3(OH)_3(COOH)_2$) differs from pyrogallol in that it contains two benzene groups; still, these compounds are similar in that their hydroxyls are in adjoining positions. Tannin was found to be a more satisfactory addition-agent than pyrogallol, so it may be said that the two extra hydroxyl radicals in the tannin is what causes more satisfactory deposits from not only lead fluo-silicate and copper fluo-silicate electrolytes, but also the deposits from electrolytes of copper sulphate and lead nitrate.

The chemical structure of gelatine cannot be compared with that of either tannin or pyrogallol, as its composition is not fully known. The only thing in common is that gelatine is composed of groups of benzene rings, which contain hydroxyl and amino-radicals. Whether it is the larger number of hydroxyl and, as well, the amino-radicals of the gelatine, which is the cause of the formation of the most satisfactory deposits of lead, copper and silver from their respective electrolytes, when gelatine is the addition-agent, remains to be proven.

With these generalities in mind, it may be said: That the most suitable organic addition-agents for lead, copper and silver electrolytes are compounds of the benzene ring series, which have a large number of adjoining hydroxyl radicals; and also, the greater the molecular weight of the addition-agent (or, in other words, the larger the number of hydroxyls), the more effective it is in producing more satisfactory deposits.

If it is the hydroxyl (and, as well, the amine) radicals of organic addition-agents which causes deposits to form denser, smoother and less crystalline, then no doubt this effect may be attributed to the reducing property of the addition-agents. This statement was suggested by recalling a general rule of organic chemistry, which is: "The most easily oxidizable organic compounds of the benzene ring series, and those which more readily

precipitate metals from their solutions, are compounds which contain the largest number of hydroxyl, or amine radicals; and the compounds which are most easily oxidized are those in which the hydroxyl and the amine radicals are the more closely grouped."

In the selection of an addition-agent there is no known specific property, nor characteristic chemical composition, which may be used as a guide in the selection. The addition-agent which is the most suitable one for a certain electrolyte may not prove beneficial when added to another electrolyte which contains either a similar anion or a similar cathion.

At the present time, with the lack of reliable data, the only means of selecting the most suitable addition-agent is patient experimenting. However, this general statement may be made: That the greater the molecular weight of the addition-agent, and the larger the number of adjoiningly grouped hydroxyl (and amine) radicals which the compound contains, the more effective it is in producing denser, brighter, less crystalline and more coherent deposits of lead, copper and silver.

A Theory of the Function of Addition-agents.

A theory which may be deducted from the above generalizations is that the function of an addition-agent in an electrolyte is to maintain a reducing menstruum around the cathode, which, in turn, causes the electro-deposit to form denser and smoother. In support of this theory may be cited the fact that the most dense, the least crystalline, and the smoothest deposits are, as a rule, produced in electrolytes which are composed of an anion which is not highly oxidizing, that is, oxygen is not a component of the anion. As example, confirming this statement, we have the following, given in the order of their smoother and denser depositions: Silver, gold and nickel, from cyanide electrolytes; lead, copper, nickel and silver, from fluo-silicate, fluo-borate and methyl-sulphate electrolytes; copper, iron and nickel, from sulphate electrolytes; and iron and nickel from chloride electrolytes; whereas these metals are non-coherent and very crystalline when deposited from their nitrate, chlorate or similar electrolytes.

The deposits formed in electrolytes, which contain alkali, or alkaline earth salts, are generally denser, smoother and less

crystalline than those which are formed in electrolytes which do not contain these salts. This is the case with nickel sulphate and nickel chloride electrolytes which contain their respective sodium salts, and with iron sulphate and iron chloride electrolytes which contain salts of either sodium, potassium or magnesium. The formation of smoother and less crystalline deposits from these electrolytes may be attributed to the reducing action of the sodium, potassium or magnesium ions in the layer of electrolyte which surround the cathode. Ammonium salts act similar to the alkali salts, but to a less marked degree. These facts also seem to confirm the above advanced theory.

And as further evidence may be cited: That deposits formed in electrolytes which contain free chlorine, nitric acid, chloric acid or other oxidizing agent are, as a rule, non-adherent and very crystalline; examples, nitric acid, free chlorine or potassium chlorate in electrolytes of lead, nickel, iron, copper, gold and silver, and ferric salts in iron electrolytes.

The fact that the consumption of organic addition-agents is in proportion to the amount of metal deposited is still another evidence of their reducing action. And for this reason, in order to maintain the deposition of smooth, dense, coherent deposits, the organic addition-agent must be added in definite amounts to the electrolyte from time to time. The effect of an excess of some of the more effective addition-agents is, in most cases, chemical precipitation of amorphous cement-metal, whereas when added in smaller amounts no chemical precipitation occurs, but on electrolyzing the deposits form brighter and smoother.

Whether the hydroxyl (and amine) radicals of the organic addition-agents affects the ionization of the constituents (especially the anions) of the electrolyte, and thereby alters the character of the deposited metal, is a problem for the physical chemist to solve.

Conditions Which Affect Electro-deposition.

If unsatisfactory deposits form, the cause may be attributed to one or more of the following conditions:

a. In case the metal stands above hydrogen in the e.m.f. series, free acid in the electrolyte causes rough, non-coherent deposits.

b. In case the metal stands below hydrogen in the e.m.f. series, rough, non-coherent deposition is caused by the presence of metals which stand close to or below it in the e.m.f. series.

c. The electrolyte contains anions which are highly oxidizing.

d. The current-density employed is too high.

e. The circulation of electrolyte is not sufficient to supply cathions to the layer of electrolyte surrounding the cathode as rapidly as the metal is deposited.

f. The electrolyte is too dilute, it contains too small amount of metallic salt for the current density employed.

g. The electrolyte contains suspended matter, which mechanically, and statically, collects on the cathode, and becomes a nucleus for nodular deposition, or else acts as an electric-couple and causes non-adherent deposits.

So in order to increase the density, the smoothness and the coherency of electro-deposits, the necessary conditions are:

a. For metals which stand higher than hydrogen in the e.m.f. series, neutral or alkaline electrolytes.

b. Pure electrolytes, which are free of salts of metals which stand in the e.m.f. series close to, or below the metal being deposited.

c. Electrolytes composed of anions which are not highly oxidizing.

d. A current-density which is not greater than that necessary to deposit the metal as rapidly as the cathions are supplied to the layer of electrolyte surrounding the cathode.

e. Ample circulation to keep the layer of electrolyte surrounding the cathode sufficiently supplied with cathions.

f. Concentrated electrolytes (use more soluble salts).

g. Electrolytes free of suspended matter.

h. Electrolytes at temperature between 40° and 60° C.

i. Presence of the required amount of a suitable addition-agent, either organic, or else inorganic (such as the alkali or alkaline-earth salts).

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DISCUSSION.

MR. REEVE: Mr. Chairman, I would like to say in connection with Mr. Kern's most interesting and valuable paper that perhaps the reason why bisulphide of carbon has not been more extensively used as an addition-agent in the silver potassium cyanide electrolyte, is that many have obtained unsatisfactory results on account of not adding the proper amount in a favorable manner. Mr. Kern quotes Mr. C. H. Proctor, in "Metal Industry," as finding that benzol is a more suitable agent than bisulphide of carbon, and says it should be added: One teaspoonful for each gallon of plating solution. This statement, by itself, would appear to be misleading. Mr. Proctor also says that the benzol should be "dissolved in a strong cyanide solution in the usual manner," which, I believe, is that the cyanide solution merely absorbs a small percentage of the benzol, or bisulphide of carbon, so that the solution that is added to the silver potassium electrolyte is really a very dilute solution of bisulphide of carbon, and, I presume, benzol the same.

Mr. Kern also states, on page 33 of the paper, that he finds it desirable to add the addition-agent from time to time according to the volume of work done in the bath. Experience shows, in connection with the use of bisulphide of carbon in the plating bath, that the volume of work done seems to have very little to do with it. The bath loses the effect of the bisulphide of carbon just as rapidly when it stands idle as when it is in use. This matter is very interesting indeed to the silver plating establishments, and if it could be taken up more extensively and a report made on the investigations, it would be very profitable.

PROF. S. A. TUCKER: It seems to me from what was said yesterday, and from what I have gathered in talking with others who have used addition-agents in depositing metal, that there is a distinct amount of organic matter carried over, and that that organic matter unquestionably affects the physical properties of the metal deposited.

MR. H. H. EMRICH (*Communicated*): I am at work now on some experiments on a commercial scale with addition-agents, and will undoubtedly find some points of use in this paper.

However, operations run successfully on a small scale are often worthless when run on a commercial scale, and so far I have yet to find any satisfactory addition-agent. They may make perfectly satisfactory deposits for two, three or four weeks or so, but eventually there is a breakdown or something, probably the organic molecule, and the deposit will change for the worse.

An instance of this is in the use of molasses as an addition-agent. When first used, this produced cathodes as hard and free from lumps as a half-inch boiler plate, and I drew a wire from one of them with no trouble whatever which ran 99.3 per cent. conductivity, hard drawn, on the Matthiessen scale. The cathodes rang like iron when hit with a hammer. Cathodes pulled from this solution in six to eight weeks were so brittle as to fall apart when dropped across a rail, and the deposit resembled a cocoanut fiber mat about as near as anything else, so coarse was the crystalline structure. You will understand that in the above all other conditions were kept constant, and were the same as in our regular electrolytes. This experiment was made on about 10,000 cubic feet of solution and 136 tanks. The organic matter was present in amount sufficient to require 0.045 to 0.050 gms. oxygen per 100 c.c. for oxidation.

I shall take pleasure in testing Dr. Kern's conclusions on a commercial scale.

Prof. J. W. Richards (*Communicated*): I would suggest to Mr. Emrich to test conclusions on one tank at a time, instead of on 136 at once. One tank run six months will give quite reliable conclusions and save the cost of possible failure for the other 135 tanks.

A paper presented at the Fifteenth General Meeting of the American Electrochemical Society, at Niagara Falls, Canada, May 7, 1909; President E. G. Acheson in the Chair.

ELECTROLYTIC DEPOSITION OF LEAD AND ZINC AS AFFECTED BY THE ADDITION OF CERTAIN ORGANIC COMPOUNDS.

By S. A. Tucker and E. G. Thomssen.

Both lead and zinc present certain difficulties when deposited electrolytically from aqueous solution, and with the former it is practically impossible to deposit the metal in a reguline condition from solutions of the nitrate or acetate.

The influence of organic matter has been studied and is known to affect the deposit favorably, as in the case of lead when gelatine is used.

Classen[1] has taken out a patent for the deposition of zinc and other metals with the use of certain organic compounds of the glucoside class, claiming that the deposit is much improved, and in the case of zinc the metal comes from the bath in a bright polished condition.

The present investigation had for its object the study of the deposits of these metals with the addition of organic compounds, as recommended by Classen.

Any glucoside will be favorable to the metal deposit, according to Classen, but as a material he advises licorice root or extract, as being a cheap substance and one readily obtained.

From some preliminary experiments it was found that the addition of licorice had a very marked effect on deposits of lead or zinc. With lead from an acetate or nitrate bath, the metal could be deposited on copper in a beautiful condition, and with zinc from a sulphate bath the metal was obtained in a bright and, in certain cases, a polished condition.

The experiments were taken up with a view to determine the influence which the organic matter had upon the ratio of metal actually deposited and that theoretically possible, a study of the

[1] U. S. Pat. No. 809,492; Jan. 9, 1906.

voltage and current density, and certain changes which occurred in the electrolyte.

In the following experiments anodes of the metal to be deposited were used, the cathodes being of smooth copper, anode and cathode having an area of 50 sq. cm. each:

TABLE I. LEAD—LICORICE ROOT.

Electrolyte: 100 grams lead nitrate, 500 c. c. water.

No.	Per cent. Licorice	Voltage	Current Amperes	Current Density Amperes per square dcm.	Theoretical Deposit Grams	Deposit Obtained Grams
1	0	2.5	0.66	0.33	Deposit Non Adhesive	
2	1	2.05	0.51	0.252	0.4957	0.5047
3	2	2.05	0.51	0.252	0.4957	0.5217
4	3	2.2	0.51	0.252	0.4957	0.5342
5	0.2	1.6-1.75	0.75	0.375	0.7290	0.9448
6	1	1.4	0.49	0.245	0.4802	0.4810
7	2	1.8	0.7	0.35	0.6806	0.9981
8	3	2.0	0.82	0.41	0.7070	0 8704
9	4	2	0.89	0.445	0.7751	0.9669
10	5	1.6	1.07	0.535	1.040	1.2020

TABLE II. LEAD—LICORICE ROOT.

Electrolyte: 100 grams lead acetate, 500 c. c. water.

11	1	3.5	0.53	0.265	0.5161	0.9103
12	2	3.5	0.41	0.205	0.3985	0.4167
13	3	2.5	0.26	0.130	0.2527	0.2835

TABLE III. LEAD—EXTRACT LICORICE.

Electrolyte: 100 grams lead nitrate, 500 c. c. water.

14	1	0.5	1.11	0.555	1.0780	1.0360
15	3	0.44	1.12	0.56	1.5876	1.0334
16	3	0.62	0.53	0.265	0.5161	0.7896
17	5	0.4	1.11	0.555	1.0780	1.1237
18	5	0.22	0.40	0.20	0.3888	0.3897

TABLE IV. LEAD—EXTRACT LICORICE.

Electrolyte: 100 grams lead acetate, 500 c. c. water.

No.	Per cent. Licorice	Voltage	Current Amperes	Current Density Amperes per square dcm.	Theoretical Deposit	Actual Deposit
19	1	0.46	0.3	0.15	0.2916	0.2953
20	3	0.46	0.29	0.145	0.2818	0.2789

TABLE V. ZINC—LICORICE ROOT.

Electrolyte (according to Classen):

100 grams zinc sulphate.
20 " sodium sulphate.
5 " zinc chloride.
2.5 " boric acid.
500 c. c. water.
25 grams licorice root (added gradually).

21	1	0.36-0.4	0.8	0.4	0.2476	0.2537
22	2	0.32-0.35	0.88	0.44	0.2724	0.2765
23	3	0.3	0.87	0.435	0.2683	0.2820
24	4	0 26	0.89	0.445	0.2755	0.2810
25	5	0.26	0.88	0.44	0.2724	0.2776

TABLE VI. ZINC—EXTRACT LICORICE.

26	1	0.6	0.69	0.345	0.1136	0.1688
27	2	0 3	0.99	0.495	0.3065	0.3107
28	3	0.38	1.14	0.57	0.3427	0.3245

These experiments show that in the case of both lead and zinc the deposit actually obtained exceeded that of theory in nearly every instance. Of the two substances used, the licorice root gave higher results than the extract. The extract of licorice also gave better deposits than those obtained with the root.

The deposits in every case were exceedingly good, adhering firmly if the cathode was perfectly clean at the start and if the current density was not too high. The lead comes out unpolished, but with zinc, if the cathode is first polished, a bright coat of zinc is obtained.

When heated, the lead adheres until it fuses while the zinc becomes brittle and peels off readily.

It is impossible to raise the current density to any great extent without impairing the deposit. With 2 amperes per sq. dcm. the deposits become dark, rough, and non-adherent. The best results were obtained with a current density of about 0.5 ampere per sq. dcm.

As might be expected, the addition of the organic matter increases the resistance of the bath considerably. The resistance drops, however, to some extent after the bath has been in use for some time.

With lead, the acetate bath has a much higher resistance upon the addition of licorice than the nitrate. The resistance of the zinc bath is less than that of either of the lead baths used.

The following experiments were undertaken to investigate the increased weight of deposit obtained over that theoretically possible. Several deposits of lead and zinc were made, the deposit stripped off after weighing, and the lead and zinc determined by analysis.

The results obtained are as follows:

Deposit obtained from—

Acetate Bath with 5 Per Cent. Licorice Extract.

Weight metal deposited.	Weight metal deposited Theoretically.	Weight metal determined by analysis.
0.6665 gram.	0.6532 gram.	0.6474 gram.

Nitrate Bath, 3 Per Cent. Licorice Extract.

1.6700 grams.	1.6162 grams.	1.5197 grams.

Zinc Bath, Bath According to Classen.

1.0148 gram.	0.9904 gram.	0.9653 gram.

From this it is evident that a considerable quantity of organic matter is carried over with the metal deposited.

In order to determine the quantity of organic matter entrained, the deposit was made in the usual manner, and after washing was weighed, next it was ignited, and whatever organic matter was present volatilized at a low temperature. After cooling it was again weighed and the amount of organic matter determined by difference.

The results obtained in this manner are as follows:

TABLE VII. LEAD FROM LEAD NITRATE BATH.

No.	Per cent. Licorice Extract Added	Weight Lead Before Ignition. Grams	Weight Lead After Ignition. Grams	Weight of Organic Matter. Grams	Per cent Organic Matter
29	1	0.9965	0.9945	0.0020	0.2
30	1	2.5250	2.5212	0.0038	0.16
31	1	1.9011	1.8978	0.0033	0.17
32	1	1.8453	1.8409	0.0044	0.25
33	1	1.2571	1.2528	0.0043	0.35
34	2	1.3173	1.3121	0.0052	0.39
35	2	1.0696	1.6062	0.0034	0.30
36	2	0.2074	0.2040	0.0034	0.16
37	2	0.2347	0.2318	0.0029	0.13
38	3	6.8664	6.7248	0.1416	2.0
39	3	5.0095	4.7598	0.3497	6.0

TABLE VIII. ZINC FROM CLASSEN'S BATH.

40	1	1.4498	1.4249	0.0249	0.2
41	2	0.8084	0.8033	0.0051	0.6
42	3	0.4809	0.4764	0.0045	0.9
43	3	0.5478	0.5234	0.0244	4.0

An examination of these figures led to more definite information concerning the amount of organic matter which is taken over in the deposition of these metals. In a fresh bath very little, generally less than two-tenths of a per cent., is found in the deposit. As the bath grows older more is found. Numbers 29 to 33 where 1 per cent. of the licorice extract was used show this plainly. The maximum amount of organic matter carried over was arrived at in No. 39 in the case of lead. The bath had been used for nine hours. At the end of this time the deposit of lead was very poor, being rough, non-adhesive and black. The same thing was true of zinc in No. 43, where 4 per cent. of the organic substance was found. The bath in this experiment had been used for fourteen hours.

In obtaining thick deposits of lead or zinc, it was found that, in using a bath for a long time, the deposit at the end of several hours became very poor. If such a deposit is scraped it can be

seen that the metal first deposited is very good, and as the time goes on it becomes poorer and poorer until it no longer adheres. This is entirely due to the bath itself, and not to the thickness of the deposit, for a new cathode introduced into the bath gives the same poor deposit of the metal.

It was observed, however, that if more of the licorice is added to the bath when it is in this condition it again becomes as good as when it was fresh; stirring also has a tendency to produce the same effect. In order to secure a good thick deposit of the metals it is advisable to add the organic matter gradually and to keep it well stirred.

It was also found that the amount of organic matter carried over with the metal increased with its contents in the bath. This is shown by comparing Nos. 29 and 34. Licorice extract was used in obtaining this data in preference to the root, as it was found to give better deposits and, with its use, less organic matter is carried over to the cathode.

A series of experiments were next made, using a rotating cathode with electrolytes of the same composition as used with stationary electrodes. The speed of rotation was from 600 to 2,000 r. p. m., and it had the usual effect on the deposit that the rotation of the cathode during electrolysis brings about.

In some cases the current density could be increased 90 times over that with a stationary electrode, and with both lead and zinc the deposits were greatly improved.

The quantity of organic matter carried over with the metal is about the same as before and this quantity depends upon the age of the electrolyte, as was before noted.

The deterioration of the bath takes a longer time with a revolving cathode, which is probably due to the stirring effect of the electrode.

In the deposit of zinc it was found that zinc sulphate alone, with the addition of licorice, gave quite as good results as when the electrolyte was made up with the additions as recommended by Classen.

Electrochemical Laboratory, Columbia University,
March, 1909.

DISCUSSION.

MR. CARL HERING: In this connection I would like to call attention to a paper I read before the Society several years ago,[1] in which I showed that as a result of experiments made by Dr. Northrup and myself under the microscope, particles which are non-conductors also travel with the real electric ions, and it seems that this might be a possible explanation of the phenomenon that Prof. Tucker has noticed. It seems that those particles of licorice, if they are colloids, that is, if they are visible particles under the microscope, they will follow the law that seems to be true of all such particles, namely, that they also travel with (or against) the current, and therefore are deposited on the cathode (or anode) together with the metal of other ion.

PROF. S. A. TUCKER: I might say in answer that Mr. Northrup gave me an explanation to account for the action of the organic matter, which depends on the migration of the particles towards the cathode when the electric current is passing, as he has observed under the microscope. If the cathode has a projection or nodule, the organic particles will naturally be carried to it first, and as it has a higher resistance than the metal, it will tend to cover over the projection, allowing the metal to be deposited around it on the other portions of the cathode, which will ultimately become a smooth surface.

MR. HUGH RODMAN: Dr. Tucker believes the electrolytic lead likely to be of use in storage battery construction. It may be of interest to say that electrolytic lead deposited from Bett's solution has proven unsatisfactory for this service. While the deposited lead is somewhat stiffer and, therefore, better from a mechanical standpoint, it is apparently more liable to chemical and electrochemical attack. This characteristic renders it peculiarly unsuitable for Plante positive plates where the densest and most resistant lead is necessary.

[1] Visible Migration of Particles between Electrodes. Hering. Trans. Am. Electrochem. Soc. Vol. X p. 35.

A paper presented at the Fifteenth General Meeting of the American Electrochemical Society, at Niagara Falls, Canada, May 7, 1909; President E. G. Acheson in the Chair.

THE ELECTROLYTIC PRODUCTION OF WHITE LEAD.

By Jno. A. Yunck.

In considering so important a commercial product as white lead, one asks: Is it possible to produce it electrolytically at a price and of a quality to compete with other existing methods? To make it useful to the arts and commerce it must stand on equal footing with the purely chemical product. That which has been done to the present day was largely experimental, though very much has been tried and various methods improved, but it has not been applied commercially, to my knowledge.

The writer has experimented for some years, and operated a small plant making about 50 pounds of white lead each day, for several months. The actual time consumed each day for corrosion was about five hours. In the course of our experiments, we tried a great many forms and variety of shapes of electrodes, both anodes and cathodes, also large number of solutions, of varying densities, and at various temperatures, as well as of physical conditions. Another important factor considered was the current densities, or amperes per square foot of anode surface; still another was to have the cathodes of about the same resistance as the anodes, and keeping the condition of the electrolyte at as near a uniform temperature as possible.

By this way we were enabled to produce white lead equal to the best for covering and color qualities. The experiments referred to were conducted at the laboratories of the late Rev. John B. Tibbits, at Hoosick, N. Y. The apparatus consisted of a tank about 36 inches high, by 24 wide and 30 inches long (with glass sides to note the operation). On the top of the tank were suitably arranged copper conductors to which the anodes of lead and cathodes of aluminum were fastened. At first we used solid lead plates about ¼ inch thick, 24 inches long and 12 inches wide, and

cathodes nearly the same dimensions. The distance between the plates was about ½ inch; this worked very well for a time, but owing to improper circulation of the electrolyte local action soon set in and heated the solution so that the production slackened, and we found it necessary to stop to cool off the solution.

We arranged the tank so as to have running water surrounding it to keep it cool, and at the same time placed in the bottom of the tank a device which kept the solution in a slow steady motion. We cast the anodes and cathodes in strips or grids connected at top and bottom. After that we were enabled to continue the operation continuously. We used for an electrolyte two solutions, one of a 15 per cent. solution of nitrate of soda, the other of nitrate of ammonium. The first was cheapest in first cost, though in the opinion of the writer ammonium nitrate being a better conductor, it would be cheaper from a commercial standpoint to use it. During the corrosion carbon dioxide gas was allowed to pass through the electrolyte from small orifices at the lower part of the tank. After running for about 2½ hours, we stopped the operation for about ½ hour to allow thorough settling, the solution was drawn off, and the precipitated white lead was removed, washed and dried. The current used was 10 amperes per square foot anode surface, and from 1 to 2 volts.

As the electrolytic solution is made up of sodium and ammonium nitrate in water, and the solution is saturated with free carbon dioxide, the reaction taking place upon passage of the current can be described as follows: The solution is decomposed, yielding at the anode nitrogen pentoxide, ozone and oxygen, and at the cathode, sodium hydrate, ammonium and hydrogen. The lead is attacked by the powerfully oxidizing nitrogen pentoxide (N_2O_5) and ozone; since nitrogen pentoxide in the presence of water is decomposed and forms nitric acid.(HNO_3.)

During the double decomposition which takes place, nitric acid (HNO_3) and hydroxide of lead, Pb $(OH)_2$ are formed. The nitric acid combines with the free ammonia and sodium hydrate to again form sodium nitrate, while the plumbic hydrate is precipitated by the free carbon dioxide present and forms finally the hydrated carbonate of lead $2PbCO_3 + Pb(OH_{,2}.)$ Thus it is seen that although the solution is decomposed by electrolysis, it

is regenerated by the chemical reactions taking place, and the only materials consumed are some lead, carbon dioxide and water.

By this process we produced a white lead that was finer than can be ground by any mechanical means, and the finer the particles the greater the covering properties. The best commercial white lead contains the greatest amount of water, the amount running up to 2 per cent. This quality is more or less difficult to obtain ordinarily, but in the electrolytic process it is very easy, furthermore this process produces the lead in a very finely divided state. There is no way at the present time open or known to the chemist by which white lead can be made or produced without free carbon dioxide.

One hundred pounds white lead is composed of about 80 pounds metallic lead, 12 pounds carbon dioxide, 2 water and 6 oxygen, forming an oxy-carbonate of lead. Pure carbonate of lead is unfit for painting purposes; the combination with the oxide and water renders it much more opaque and therefore of greater covering qualities.

Now comes the question from a commercial standpoint: Can we produce this product at a profit to the manufacturer? This can be answered, yes.

The current cost for a ton of white lead would be about 500 kilowatt hours; the cost of such materials as nitrate of sodium or ammonium could be counted as a fixture, because they are regenerated with only the slight loss that is due to the washing of the precipitate. The only loss is the water and a small amount of the carbon dioxide. The installation of a plant costs very much less than old methods, which involve the enormous outlay of the old corroding process, where capital is idle for months, not earning anything. The electrolytic method can convert metal into the carbonate from day to day. The health of the operators should also be taken into consideration; as this method can be worked so automatically that the human hand need not come in contact with the product, as most of this operation is conducted under water. I have worked still another process, somewhat similar to the one described, with exception that the carbon dioxide is generated simultaneously with the precipitation. The writer will make this the subject of another paper.

As to the production of colors, where the anodes are composed

of bimetallic substances, lead in combination with copper, nickel or iron, and whereby various colors and shades are produced, this is a large subject with which I am unable to deal fully this time, but will do so in the near future. Colors of the most delicate shades and tints can be produced, of different kinds, with ease. The precipitation being uniform when different electrodes and electrolytes are used, iron oxide paints of particular richness in texture as well as color are produced this way, and very cheaply. The writer has on exhibition some specimens made some years ago, of both white lead and colors.

DISCUSSION.

PROF. BURGESS: Mr. Chairman, I am wondering whether the writer has told us all the difficulties which would be encountered in operating a process of this sort. As I remember the paper from reading it over, it stated that there was no consumption of materials other than the lead and carbon dioxide in the production of lead corbonate, and that in the use of sodium nitrate and of ammonium nitrate solutions these materials are regenerated. As a matter of fact, in electrolyzing a solution of this sort for any length of time, there will be an accumulation of hydroxide in the electrolytic due to reduction to ammonia, consequently a loss; it is difficult to prevent formation of a plumbate by redissolving of some of the lead precipitate, giving rise to a deposition of spongy lead at the cathode. Further than this, there is an oxidization of the anode, which does not produce a clean, uniform corrosion, resulting in a separation of the particles of peroxide of lead, lead scale and other impurities, which will contaminate the product. Operating a cell of this sort, it has been my experience that you get anything but a desirable appearing quality of white lead. The limitations of the electrolytic process are discussed in Vol. III of the Transactions of this Society, pp. 300-316.

A paper presented at the Fifteenth General Meeting of the American Electrochemical Society, at Niagara Falls, Canada, May 8, 1909; President E. G. Acheson in the Chair.

RAPID ELECTROCHEMICAL ANALYSIS: A COMPARISON OF SEVERAL METHODS

By L. S. Palmer and R. C. Palmer.

Introduction: Considerable literature has appeared in recent years on the rapid deposition of copper, zinc and other metals. Various devices have been employed such as rotating the cathode, rotating the anode and lately even rotating the electrolyte. Some experiments on the determination of copper with the apparatus of Frary[1], in which the electrolyte is rotated and the electrodes are stationary, led us to believe that the speed with which complete deposition was obtained was not wholly accounted for by the fact that the electrolyte rotated, but depended to a large extent upon the nature of the electrodes. The anode used in the Frary apparatus is a platinum spiral of about 1 mm. diameter; the cathode a platinum gauze, weight about 14 grams, 15 mesh to 1 cm., size 11 by 5 cm.

To test this supposition we conducted a series of tests to determine the relative merits of the two factors: gauze cathode and rotating electrolyte, in rapid depositions.

Plan of Work: Three sets of tests were made with cupric sulphate solutions—one with a rotating electrolyte using the gauze cathode; a second set without rotation of electrolyte using a gauze cathode; and for comparison a series using the usual form of platinum cone as cathode, without rotation of the electrolyte.

Two sets of tests were made on zinc depositions similar to the first two for copper, with the exception that the electrolyte was cooled by means of water flowing through a lead spiral surrounding the vessel containing it, as described by Frary.[2]

[1] Jour. Amer. Chem. Soc., 29, 1592 (1907).
[2] *Loc. cit.*

The conditions for the copper determinations were taken from data given by Fischer.[3] The conditions for the zinc depositions were taken from data given by Frary.[4]

At the end of each experiment the solution was siphoned off with the current still on and water added to dilute the electrolyte to prevent the re-dissolution of the deposit. The first 250 c.c. portion was saved for testing the completeness of the deposition by means of the usual potassium ferrocyanide test.

In the zinc determination, in place of a nickel gauze cathode as described by Frary[5], the cathode was plated with copper before each determination.

Results: The data obtained are presented in Tables I and II, and the essential results are represented graphically in Figures 1 and 2. The curves show the quantities of deposit as a function of the time of electrolysis in minutes.

TABLE NO. I—COPPER DETERMINATIONS.

Magnetic Rotation of Electrolyte—Gauze Cathode.

Test No.	Time Minutes	Current Amperes	Copper Taken Grams	Copper Deposited Grams	Copper Deposited Per cent.	Volume of Electrolyte c. c.	HNO_3 (*a*) in Electrolyte c. c.	Cu. in. Sol. after Electrolysis.
1	$2\frac{1}{2}$ to 3	$4\frac{1}{2}$ to 5	0.310	0.1178	38	130	20	. . .
2	5	"	"	0.1774	57.22	"	"	. . .
3	7	"	"	0.2377	76.99	"	"	. . .
4	12	"	"	0.2792	90.06	"	"	. . .
5	15	"	"	0.3000	96.77	"	"	test
6	20	"	"	0.3074	99.13	"	"	test
7	25	"	"	0.310	100	"	"	none
8	30	"	"	0.310	100	"	"	none
9	60	"	"	0.310	100	"	"	trace
10 (*b*)	62	"	"	0.3073	99.12	"	"	test

(*a*) HNO_3 Sp. Gr. (1.2).

(*b*) In this case the cathode was removed without siphoning off the electrolyte, the result showing that this point in the manipulation is essential.

[3] "Elecktroanalytische Schnellmethoden," p. 106.

[4] Jour. Amer. Chem. Soc., 29, 1596 (1907).

[5] Jour. Amer. Chem. Soc., 29, 1596 (1907).

Without Rotation of Electrolyte—Gauze Cathode.

1	10	4½ to 5	0.310	0.1787	57.64	130	20	. . .
2	20	4½ to 5	"	0.2646	85.35	"	"	. . .
3	33	4	"	0.2949	95.13	"	"	test
4	40	4	"	0.3066	98.90	"	"	test
5	50	4½ to 5	"	0.3100	100	"	"	trace

Without Rotation of Electrolyte—Cone Cathode.

1	30	4½ to 5	0.2398	0.1008	42.4	130	20	much
2	2 hrs.	"	"	0.2184	91.1	"	"	much
3	5 hrs.	"	"	0.2398	100	"	"	trace

TABLE NO. II—ZINC DETERMINATIONS.

Magnetic Rotation of Electrolyte—Gauze Cathode.

Test No.	Time Minutes	Current Amperes	Zinc Taken Grams	Zinc Deposited Grams	Zinc Deposited Per cent.	Volume of Electrolyte c. c.	NaOH in Electrolyte Grams	Zinc in Solution after Electrolysis
1	7½	4.5	0.1012	0.0744	73.5	100	8	much
2	15	4.5	"	0.1005	99.3	"	"	test
3	25	4.2	"	0.1009	99.6	"	"	test
4	30	4.5	"	0.1012	100	"	"	trace

Without Rotation of Electrolyte—Gauze Cathode.

1	7½	4.5	0.1010	0.0787	77.9	100	8	test
2	15	4.1	"	0.0915	90.59	"	"	test
3	25	4.5	"	0.1003	99.3	"	"	test
4	30	4.1	"	0.1010	100	"	"	none

Discussion of Results: The first table shows that under the conditions of our experiments 0.31 gram of copper was completely deposited on the gauze cathode in twenty-five minutes with magnetic rotation of the electrolyte; in fifty minutes without rotation and in five hours using the platinum cone cathode. That is, the copper was deposited twice as fast with rotation as without, and twelve times as fast with rotation as by the old cone

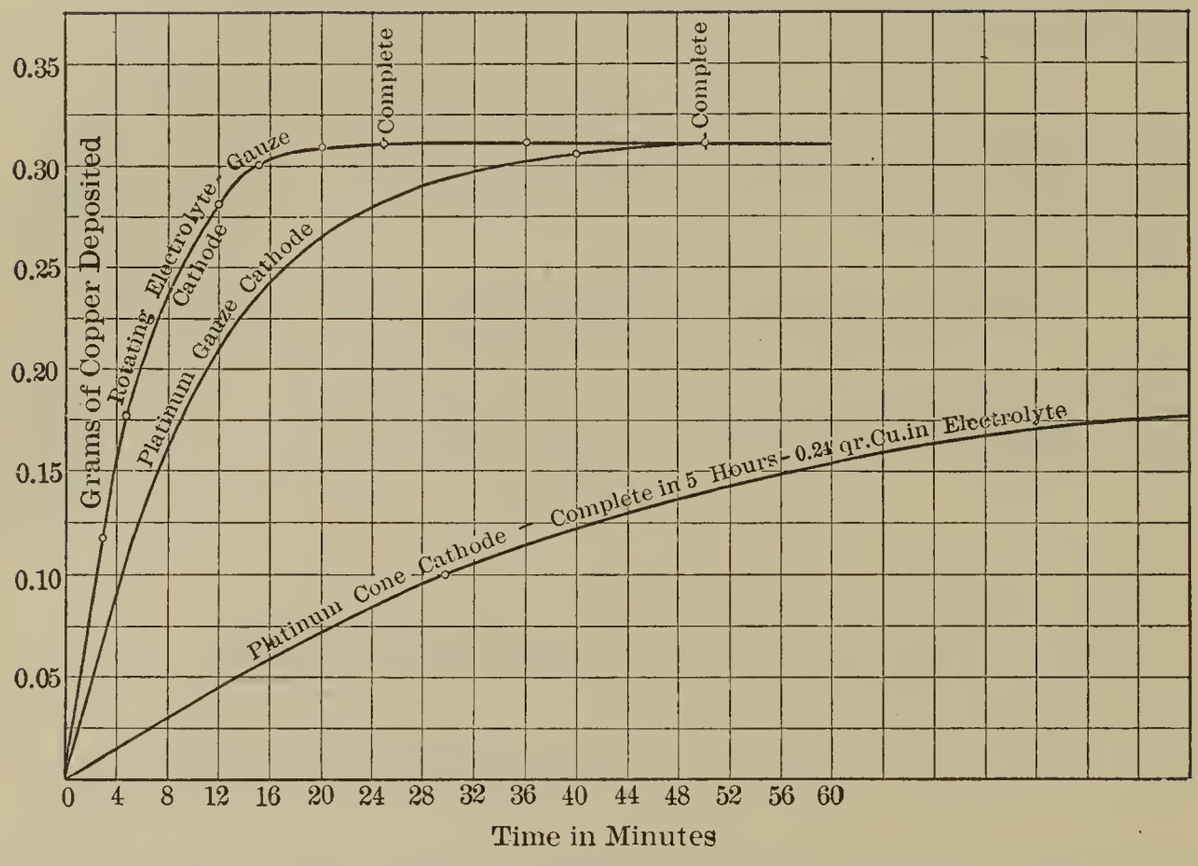

Grams of Copper Deposited
0.35
0.30
0.25
0.20
0.15
0.10
0.05
Complete
Complete
Rotating Electrolyte-Gauze Cathode
Platinum Gauze Cathode
Platinum Cone Cathode — Complete in 5 Hours - 0.24 gr. Cu. in Electrolyte
0 4 8 12 16 20 24 28 32 36 40 44 48 52 56 60
Time in Minutes

FIG. 1

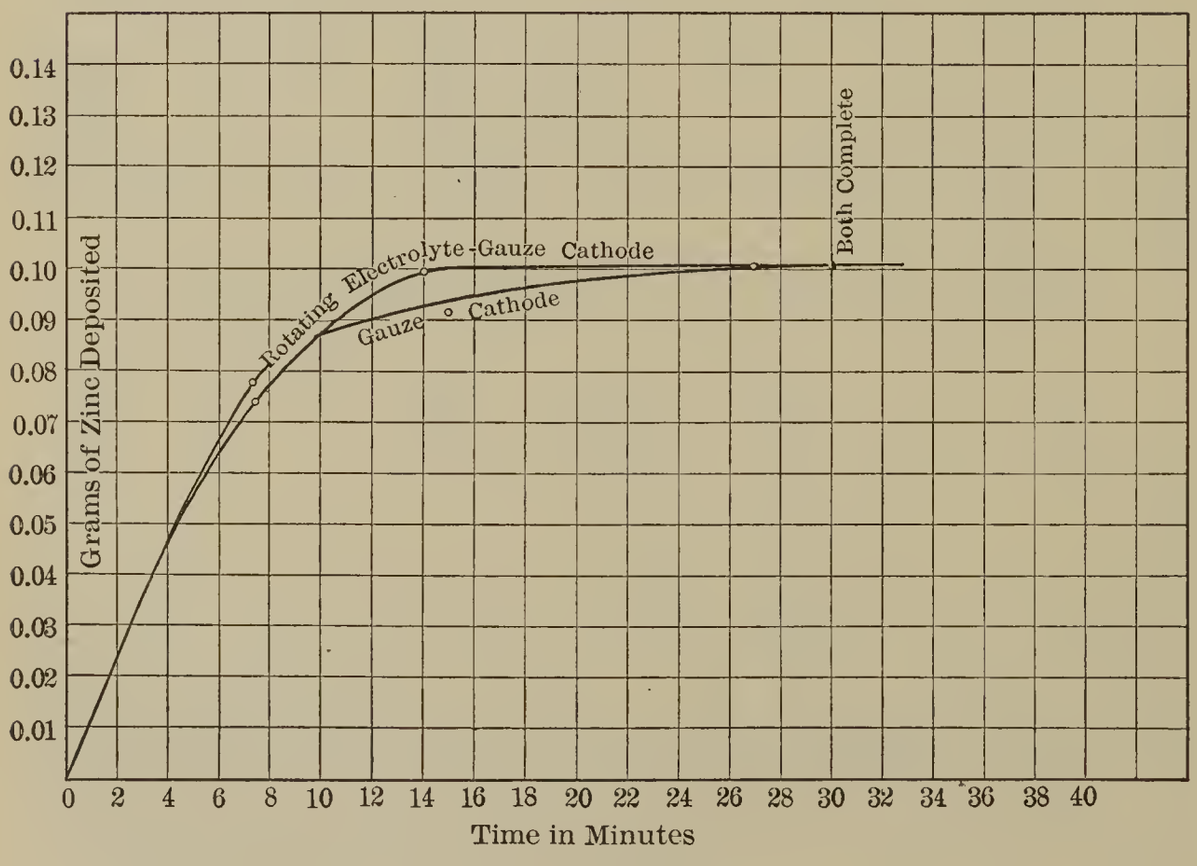

Grams of Zinc Deposited
0.14
0.13
0.12
0.11
0.10
0.09
0.08
0.07
0.06
0.05
0.04
0.03
0.02
0.01
Both Complete
Rotating Electrolyte-Gauze Cathode
Gauze Cathode
0 2 4 6 8 10 12 14 16 18 20 22 24 26 28 30 32 34 36 38 40
Time in Minutes

FIG. 2

method. It seems from this that the rapidity of Frary's method is due, in a large measure, to the gauze cathode. (See curves, Fig. 1.)

Another test was made which showed the marked influence of the gauze cathode on rapid deposition, in which, without rotation of electrolyte, 0.5 gram of copper was completely deposited on a platinum gauze from 50 c.c. of solution, in five minutes. A current of 8 to 10 amperes was used with only a few drops of conc. nitric acid. The deposit, however, was slightly spongy.

The two sets of data in Table II show no difference in the time required for complete deposition of zinc. The only difference shown is that the bulk of the zinc was deposited slightly faster with rotation. Figure 2 shows this clearly. Since Frary's result (the deposition of 0.1 gram in 30 minutes) was reproduced in both cases, we concluded that the lead coil reduced the rotation of the electrolyte to such a large extent that the slight rotation that might still exist had very little effect on the rate of deposition. In fact, there was such a large evolution of gas during the electrolysis that it was difficult to tell whether the electrolyte rotated or not, showing that there was sufficient agitation of the electrolyte from this cause alone to produce the rapid deposition.

Summary.

The use of the gauze cathode in rapid electrolytic determinations is shown by these tests of the efficiency of Frary's rotating electrolyte apparatus, to play a sufficiently important part to warrant its use alone for simple rapid determinations, and thus dispensing with the various mechanical devices for agitation of the electrolyte.

This is practically the same conclusion reached by Mr. J. T. Stoddard[6], whose paper appeared after the completion of our experiments.

Chemical Laboratory,
University of Missouri.
March, 1909.

[6] Jour. Amer. Chem. Soc., **31**, 385 (1909).

DISCUSSION.

MR. F. C. FRARY (*Communicated*): It will be a very good thing if this paper and the one by Stoddard (*loc. cit.*) serve to call the attention of American chemists to the great advantages which the gauze cathode has over all others. These were first emphasized by Paweck,[1] and later by Winkler[2] and others, who make the same point as Messrs. Palmer and Stoddard, that more rapid deposition at a higher current density is possible with its use. Its good points are clearly pointed out by Foerster[3] and Classen,[4] and mentioned by Smith,[5] but do not seem to be generally appreciated.

It seems to me, however, that the conclusion drawn from this paper and that of Stoddard, that we may dispense entirely with the rotation of the electrolyte, is premature and rests on too slight an experimental foundation. Copper is probably the easiest known metal to deposit with approximate completeness in an adherent form. That such results may be obtained even without the gauze cathode is shown by a paper read by Professor Exner before the Minnesota Section of the American Chemical Society in 1907 (but not yet published to my knowledge). He showed that copper could be satisfactorily precipitated on a platinum cylinder with stationary electrodes in a short time, by simply heating the solution from beneath with a flame, so that convection currents stirred in a little. Great results were hoped for from this method, but do not appear to have materialized.

It seems very probable that 0.3 gm. of copper could be as satisfactorily deposited from the electrolyte used by the Messrs. Palmer upon a platinum dish, without rotation, by 5 amperes in fifty minutes, as upon the gauze electrode. The ordinary cone or cylinder could not be expected to yield such results on account of the large portion of the solution which is out of the direct line of current flow. But the electrolyte used is hardly the most suitable for the rapid complete precipitation of copper. Withrow[6]

[1] Chem. Ztg. 1900, **24**, 854; Bericht über den III internationalen Congress für angewandte Chemie, Wien, 1898, Vol. 1, p. 202.
[2] Berichte 1899, **32**, 2192.
[3] "Elektrochemie wässeriger Lösungen," 1905 edition Vol. 1, pp. 238, 239.
[4] "Quantitative Chemical Analysis by Electrolysis," 1903 translation pp. 114, 115.
[5] "Electro-analysis" 1907 edition, p. 72.
[6] J. Am. Chem. Soc., 1908, **30**, 381.

has shown the retarding effect of large amounts of nitric acid; it may also be seen by a comparison of results obtained here with those given in this paper. Students here regularly get complete precipitation of 0.2 to 0.6 gm. of copper in twelve to sixteen minutes with the use of a current of 5 amperes and magnetic rotation of the solution, as against twenty-five and fifty minutes found necessary by the Messrs. Palmer with and without magnetic rotation respectively. We use an electrolyte containing, aside from copper sulphate, from 10 drops to several c.c. of concentrated sulphuric acid, and about 2 gm. of ammonium sulphate. The deposits are a little darker than those from a nitric acid solution, as stated by Winkler (*loc. cit.*), but are adherent and apparently of proper weight.

It is also doubtful whether the Messrs. Palmer obtained complete precipitation of copper in any experiments reported here if, as appears from the paper, this was determined by the use of a ferrocyanide solution. Our experience here indicates that quantities of copper in excess of a milligram are often not indicated by this reagent. Hydrogen sulphide seems to be the best precipitant.

The precipitation of zinc, as described here, is more to the point, but the conclusion that the lead coil largely reduced the rotation of the electrolyte is probably erroneous, since lead, water and air have practically the same permeability.[7] The authors were undoubtedly deceived by a phenomenon which I have frequently observed with this apparatus, that the surface of the liquid becomes partly covered with foam or froth, which attaches itself to the electrodes and does not rotate much for two reasons: (1) High electrical resistance, due to its porous structure, so that it carries practically no current and hence is subject to no torque; (2) sufficient adhesion to the electrodes, due to surface tension, to prevent it from being carried around by the moving solution. This phenomenon is especially common in alkaline solutions.

The paper of Stoddard (*loc. cit.*) is inconclusive in its present form and can not be cited in support of the conclusion mentioned, since he neglected to show in any case:

1. That precipitation was complete. He states that such was

[7] Standard Handbook for Electrical Engineers, 2, 30.

the case, but does not determine the accuracy of his methods of testing.

2. That the precipitate was of proper physical character. In the case of zinc his description shows that it was not.

3. That it represented the actual amount of metal in the solution, *i. e.*, was neither oxidized on account of sponginess, as is often the case with metals deposited at too high a current density, nor deficient in weight due to mechanical losses caused by the same condition.

The whole matter is worthy of a thorough investigation, preferably by several parties working independently, and I sincerely hope that it may receive such in the near future.

L. S. Palmer and R. C. Palmer (*Communicated*): We are pleased to have Mr. Frary call attention to some of the investigators that have pointed out the advantages of the gauze cathode. In regard to the copper depositions we call attention to the fact that our solutions contained considerable quantities of nitric acid. Mr. Frary states that such solutions are not the most suitable for rapid and complete deposition. As our object was not primarily to see how rapidly the deposits could be made complete, the fact that Mr. Frary and his students are able to obtain more rapid depositions with other solutions has only a remote bearing on the problem.

In the case of zinc depositions the permeability of lead, air and electrolyte, which Mr. Frary points out to be the same, has no bearing on the rotation. The rotation of the electrolyte is due to the number of lines of force or the magnetic flux through it. The lead coil introduced between the solenoid and the beaker evidently takes up a large number of these lines of force, causing a fewer number to pass through the beaker itself and thus decreasing the rotation of the electrolyte. However, the question of rotation has no bearing here, as our data show that the same results were obtained with and without passing current through the solenoid.

We believe that our experiments, limited though they are, point to the conclusion expressed in the paper, namely, that rotation may be dispensed with.

A paper presented at the Fifteenth General Meeting of the American Electrochemical Society, at Niagara Falls, Canada, May 7, 1909; President E. G. Acheson in the Chair.

THE DEPOSITION OF ALUMINIUM FROM AQUEOUS SOLUTIONS, USING ROTATING CATHODES.

By S. A. Tucker and E. G. Thomssen.

From experiments carried on with copper and other metals deposited on a rotating cathode, it is known that the current density can be raised very greatly and the nature of the deposit be generally improved.

It seemed possible that if the speed of rotation could be sufficiently increased, that the current density might be raised to such a high value that metals could be deposited from aqueous solution which under ordinary circumstances would not deposit at all.

It was determined to try the effect of a rapidly revolving cathode in the case of aluminium, as it is well known to be impossible to deposit this metal from an aqueous solution upon a stationary electrode.

High speeds of rotation are difficult to obtain, and the difficulties increase with the speed of rotation. The first experiments were therefore carried on with a cathode revolving at 3200 r. p. m., electrically driven. The electrolyte was an aqueous solution of aluminium chloride or sulphate with an anode of sheet aluminium. The cathode consisted of a brass or copper rod of five mm. diameter. No sure indication of metallic deposit was obtained, but several times a black substance was found on the cathode on quickly removing it from the bath. Various changes were made in the conditions, such as variation in the current density and increase of rotation up to 3,500 r. p. m., which gave a rather more pronounced result, but nothing that could be called a coherent metallic deposit was obtained.

By using a very concentrated or pasty solution and rotating the cathode as fast as possible with the apparatus at hand, better results were obtained—the blackening was much more marked and

was found to be invariably on the side of the cathode having the greatest peripheral speed due to the slightly eccentric motion of the revolving rod.

This gave the clue to the requirements for depositing the metal, as it indicated the necessity of higher speeds of rotation and the use of pasty solutions.

With the construction of a better bearing running at about 5,000 r. p. m., the deposits obtained were still black, but on closer inspection a trace of metal substance resembling aluminium was obtained. It was found that on quickly withdrawing the bath from the cathode which was still revolving that the deposit had a metallic luster for a moment. However, it turned black almost instantly on exposure to the air. In order to raise the speed of rotation a small air turbine was constructed which enabled a speed of about 10,000 r. p. m. to be reached.

With this apparatus much better results were obtained; the deposits on being first withdrawn from the electrolyte were metallic aluminium, but after a time tended to blacken on exposure to the air. This is probably due to the fine state of division in which it is formed at the cathode. In order to prove that the deposits obtained were really aluminium, they were carefully washed to free them from any adhering electrolyte and then dissolved in potassium hydroxide. As the deposits were very thin, a great many were dissolved in the solution in order to procure enough of the metal to subject to test. These tests left no doubt as to the certainty of the deposit obtained being aluminium.

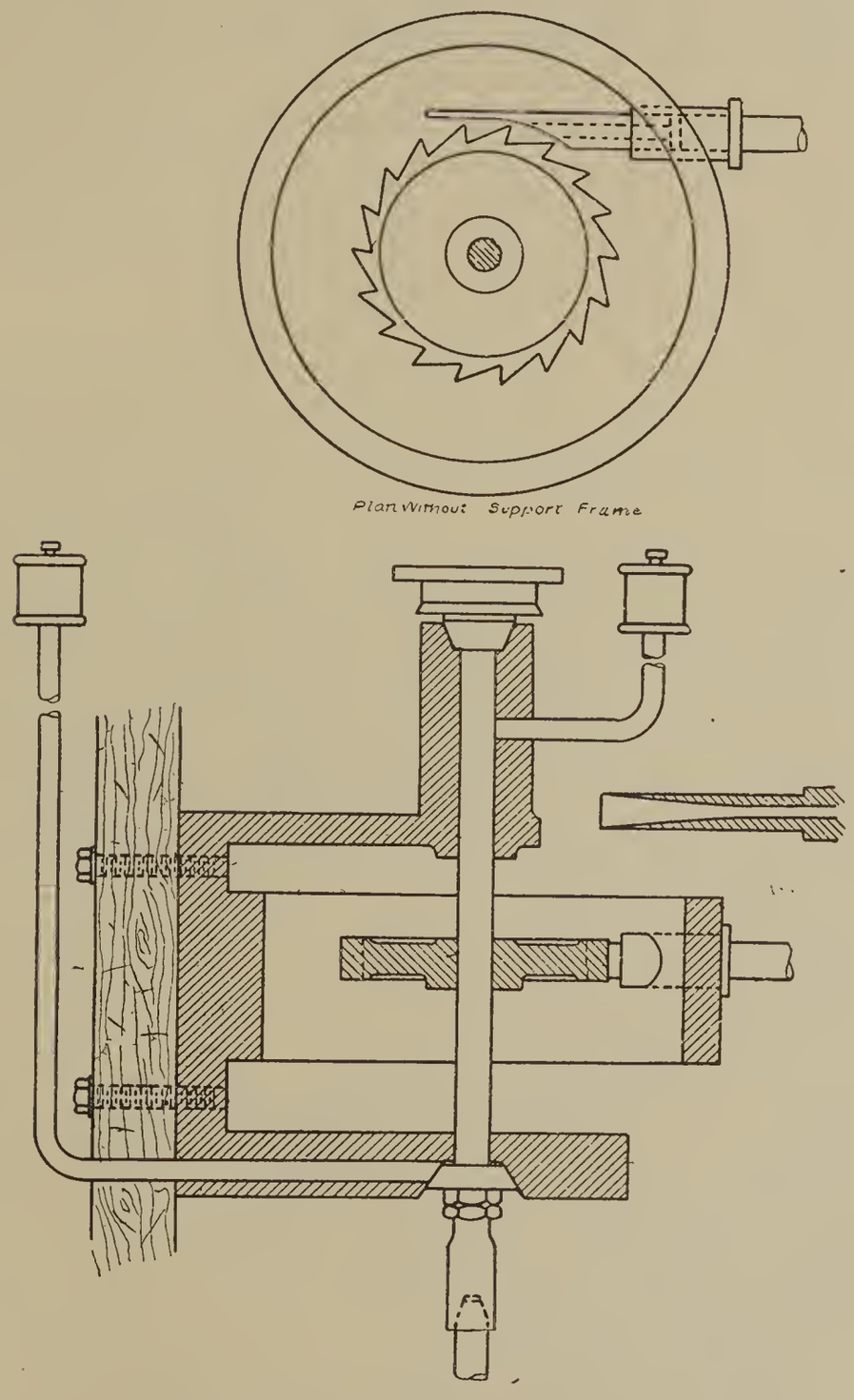
One very noticeable fact in connection with the deposit is that the aluminium obtained at the highest speed retained its metallic luster longer than when obtained at the lower speed. The blackening was hastened whenever the deposit was exposed to the air and whenever there was much water present in the electrolyte at the time of deposition.

Several of the deposits were quickly placed in melted paraffin to protect them from the air and remained bright for weeks. After standing for a few days in the paraffin there was usually no tendency to blacken on again exposing to the air.

The deposits were always extremely thin and, as before noted, invariably on the side of the cathode having the greatest peripheral

speed. In the cases where the cathode ran perfectly true the deposit completely surrounded the rod.

The temperature of the bath must also be considered in such experiments. If the temperature exceeded certain limits no



satisfactory deposit could be obtained. From a series of runs with various temperatures it was found that from 30° to 40° C. gave the best results.

The time during which the electrolysis was conducted was

for a few minutes only, since running for longer periods did not give as good results. Bad tendencies seem to increase with time. There was considerable variation in voltage and current due to change in resistance of the bath, probably due to several causes, such as formation of film, change of concentration, or vortex effect of the rapidly revolving cathode which tended to expose more or less of the cathode surface to the electrolyte.

It was thought advisable to obtain an air turbine of better construction than the one previously used, as any increase in speed would tend to give better results.

The one used was designed by Prof. Ernest F. Nichols for a different purpose, and is shown in the figure.

The apparatus was used with compressed air at 30 pounds pressure and ran with very little vibration, giving a high speed of rotation. The revolving parts cause a hum which at high speeds is a piercing high note which is far from pleasant to work with, otherwise the apparatus is entirely satisfactory.

The actual speed of rotation was estimated by comparison with a recording siren to be from 15,000 to 20,000 r. p. m.

On repeating the experiments with this apparatus the results obtained were somewhat better than before. It was found possible to burnish some of the deposits which were slightly black on a buffing lathe with rouge, the deposit then having the same appearance as polished aluminium.

The conditions under which these later experiments were conducted were as follows:

Cathode: brass, five mm. diameter.

Anode: sheet aluminium, 35 sq. cm.

Electrolyte: pasty solution of aluminium chloride.

Temperature: 30° to 40° C.

Duration of electrolysis: five to six minutes.

Revolutions of cathode per minute: 15,000.

Current in amperes: two to four.

Voltage: varied; average, 15.

Current density at anode: 0.085 amps. per sq. cm.

The deposit was only obtained on eccentric portion of the cathode, which portion had an area of 200 sq. mm., giving a current density at the actual cathode of two amperes per square cm.

The practical value of such a method for depositing aluminium

is indeed small, as the quantity of metal obtained is but a small part of that theoretically obtainable for current used.

The voltage necessary to conduct the experiments is also very high, and the practical difficulty of obtaining such speeds of rotation is very great. The experiments are interesting, however, as showing that under certain conditions it is possible to obtain aluminium by electrolysis of its aqueous solutions.

Electrochemical Laboratory,
Columbia University,
February, 1909.

DISCUSSION.

MR. F. A. LIDBURY: May I ask what tests were applied to determine its identity?

PROF. S. A. TUCKER: The deposited metal was dissolved in potash, precipitated and identified. It seemed to me that it might be possible to deposit other metals on a rotating cathode as I had done with aluminium, and a number of experiments were made with calcium, magnesium and barium. It was found, however, that there was a film effect in the case of all these metals, and with the high speeds of rotation employed that it was impossible to get a reguline deposit. I found, however, that if a sufficiently high current density was employed that a deposit was obtained on a stationary electrode from an aqueous solution of calcium chloride, which was spongy, gray and evolved hydrogen briskly on being plunged into water. I took this to be metallic calcium. Under the microscope it appeared to be metallic calcium sponge mixed with calcium hydroxide.

DR. O. P. WATTS: In regard to this last statement, that metallic calcium and barium, etc., have been obtained, mixed with hydroxide, it seems to me that is open to question. I think it has been pretty well established that in the fused electrolyte subchlorides are formed of barium, strontium and calcium, and it seems to me much more probable that in this case it was a subchloride that formed. These subchlorides will decompose water, and in that respect act like metal. So I think it is ques-

tionable whether any metallic calcium was obtained in the case mentioned.

PROF. TUCKER: I would like to ask Dr. Watts what subchloride looks like. This did look like metallic calcium, which we are all familiar with. I cannot be positive of this metallic calcium. It had the properties, the appearance, and the quick decomposition with water.

DR. WATTS: I cannot describe it from personal knowledge. I simply obtained this information from experiments given in the literature. It is usually a grayish, spongy mass obtained around the cathodes in these fused electrolytes; never a solid, adherent substance.

MR. C. A. HANSEN: It is, of course, a very difficult matter to get as great relative motion between cathode and electrolyte by rotating an immersed cathode. It would seem easier to get great relative motion by squirting solution upon the cathode and electrolyzing the stream. The limit to the relative velocity between electrolyte and cathode attainable would also be raised. This has been worked out, at least experimentally, for copper solutions.

MR. W. R. MOTT: Speaking of the deposition of aluminum, in the electrolyzing of non-aqueous solutions of aluminum chloride, I noticed an interesting phenomenon, particularly with amyl alcohol. The condensation power of the aluminum chloride was very marked. In fact, with amyl alcohol, on allowing it to stand a month or two, you can form a very excellent glue out of the condensation product, nearly as strong as the ordinary glue.

Speaking of the deposition of metals similar to aluminum, I tried the other day an experiment to deposit titanium. I dissolved some titanium out and formed a strong solution that contained essentially *only* titanium sulphate and sulphuric acid, and electrolyzed it with a fairly high current, and got a good white deposit on a copper cathode. I have not, however, analyzed that deposit to determine what percentage of titanium may be present and what percentage of iron may be present. The titanium solution was prepared from C. P. chemicals. The usual fault we find with these deposits, especially in the deposition of aluminum, is that they turn out to be not aluminum, but to be iron, and perhaps that is the case here. I wonder if any one present has

ever electrolyzed titanium solution and had deposition. It is a very interesting field.

Mr. A. H. Cowles: Years ago we performed experiments at Lockport, electrolyzing a saturated solution of sodic aluminate in water, and as a conclusion of the work we did on this we came to the decision that we could get a film of real aluminum on copper, but the moment the film formed thick enough so that the decomposition of the water on it could balance the deposition of aluminum, that film would cease to grow thicker. The subject has come up very frequently with me in the last fifteen years as to whether it is possible to deposit aluminum from a water solution. About ten years ago it was claimed by some engineer in Philadelphia that they were plating the large pieces of ornamental iron for the new Philadelphia City Hall with aluminum. In fact, our company sold to the people who were under this belief quite large quantities of aluminum for the anodes which they used in this work. I was so interested that I went to the place where the work was being done one Sunday and talked with a workman there. He explained that they melted the aluminum down with tin into anodes before they attempted the plating. I asked him if there was a white sludge left in their plating bath after they were through electroplating. He said, yes, there was a very large amount of white sludge there. From that I inferred that the City of Philadelphia had been paying for tin plating on their elaborate iron ornamentation instead of an aluminum plating.

At one time there was a sample sent to us of a plating claimed to be aluminum from a wet solution. Tests of it showed both tin and aluminum in the plating, but not pure aluminum. How that was done I do not know, but undoubtedly some one had plated out of a wet solution an alloy of tin and aluminum. These instances are the nearest I have ever come to encountering a real deposition of aluminum out of a wet solution. Impurities in the solutions quite easily lead to a white deposit which might be mistaken for aluminum when you test. Of course, I do not know the details of the experiments described in the paper. I am rather curious to know whether it may not have been the hydroxide of iron rather than alumina that came down when they tested qualitatively for aluminum.

PROF. TUCKER: I am as near sure as anyone can be that what we obtained was aluminum. In many experiments we got the metal down in smooth and yet frosty condition, perfectly typical of aluminum. I do not think for a moment you would hesitate to say it was aluminum. Chemical test showed that.

MR. WILLIAM KOEHLER: Mr. Chairman, I have lately succeeded in depositing metallic aluminum from a dilute solution of aluminum chloride slightly acid with hydrochloric acid, but the power factor is of such a nature as to prohibit the commercial success of same.

The deposition depends entirely upon holding and keeping initial conditions, viz.: A pure dilute solution of slightly acid aluminum chloride, a great cathodic speed of the electrolyte, and high cathodic density. A good semipermeable diaphragm is necessary.

By observing the above conditions closely, chlorine gas is evolved at the anode and aluminum deposited at the cathode. By high current density I have reference to a large cathodic current, so high, in fact, that hydrogen is freely evolved in larger quantities over and above metal deposition. This is necessary for the success of the operation.

I have not been able to hold the initial conditions for any considerable length of time (at the most, fifteen minutes) for the reason that oxide of alumina is readily precipitated from the solution, and this precipitate then raises the voltage to such an extent that the current becomes disrupted. The metal which I have succeeded in depositing upon a tubular iron cathode (a piece of drawn steel tubing) showed all the properties of metallic aluminum. The deposit had a metallic luster, was soluble in caustic soda with the evolution of hydrogen. The resulting caustic solution after transposition with hydrochloric acid gave with ammonia a precipitate having all the properties of alumina hydroxide, these reactions proving that the deposit was metallic aluminum.

Metallic aluminum can also be produced through the electrolysis of a dilute sodium aluminate sodium chloride solution.

The deposition of metallic aluminum from aqueous solutions can be accomplished, but the same is not a commercial possibility.

A paper presented at the Fifteenth General Meeting of the American Electrochemical Society, at Niagara Falls, Canada, May 8, 1909; President E. G. Acheson in the Chair.

A GRAPHITE CATHODE DISH

By J. W. Turrentine.

In conducting a laboratory course in applied electrochemistry, one devoted largely to that phase of electrochemistry which has to do with solutions and the electrolysis of solutions, the need has been experienced for some good material which could be substituted for platinum in the construction of insoluble electrodes. Platinum, to be sure, makes the ideal insoluble electrode, but its cost makes the matter of supplying a large class with electrodes constructed of it impracticable. The initial expense is great and the care of it is a burden on the instructor.

In the Cornell laboratories, for ordinary work, graphite has been substituted. Trouble was experienced with this material on account of the fact that it was porous and absorbed the solutions in which it was used, and, therefore, could not be cleaned readily. This prevented its use in experiments where impurities might interfere with the desired reaction. Also, at high current densities the graphite electrodes showed a tendency to disintegrate and to fill the solution with clouds of finely divided graphite powder. This was due, possibly, to the discharge within its pores and beneath its surface of gases which forced off the surface particles. A further objection was found in the graphite's propensity for rubbing off and smutting.

After experimentation to determine a means of preventing the absorption of solutions by the graphite, it was found that if the graphite electrodes were treated while hot with molten paraffin, in amounts which are readily absorbed by them, the surface of the graphite acts as though it were greased, and is not wetted by aqueous solutions. Because of surface tension phenomena, the pores are not entered by the solutions. This treatment, by keeping solutions from the pores, should also prevent the disintegration of the electrodes at high current densities; however, whether it does or not has yet to be determined. Cer-

tainly it does not when the graphite is made anode in chloride solutions, but here we have the paraffin attacked by the evolved chlorine and naturally its efficiency as a protective agent is diminished. The treatment with paraffin furthermore reduces to a minimum the inclination of the graphite to rub off, so that it is rendered quite clean and it may be handled freely without smutting.

When mention was made to the Acheson Graphite Company of the behavior of the graphite thus treated, it was found that they had employed the same means for improving their electrodes when designed for certain purposes.

In the laboratory of Wesleyan University we are now using graphite electrodes made from Acheson sheet graphite of 0.5 cm. thickness. The sheet is cut into pieces which are 15 cm. by 2.5 cm. in dimensions. One end is copper plated and a copper wire about 20 cm. long is twisted around this end and is soldered in place to the copper plate. To protect the exposed metal at this point from fumes, the end of the electrode is covered with a light coating of varnish. The graphite is then paraffined while hot. The electrodes are supported by a very simple device, which consists merely of a block of wood of sufficient size to rest across the top of a beaker. It contains two parallel slits, 2.75 cm. apart and of the proper width to admit the electrodes and to hold them snugly in position.

We were thus enabled to supplant very satisfactorily by the use of paraffined graphite the platinum sheet electrodes heretofore used in ordinary experiments in laboratory work. In electrochemical analysis, however, and separations, expediency still demanded the use of the Classen platinum dish.

The use of a graphite dish as a substitute for the platinum dish need not be confined to pedagogic electrochemistry, but should also find an extended use in commercial laboratories.

Recent developments in the field of electrochemical analysis, due to the important work of Professor E. F. Smith and his students, and other investigators, have afforded us many beautiful methods of electrochemical analysis which might well and should be used in industrial laboratories. This is especially true of those laboratories connected with metallurgical plants where some electrochemical methods are already in use. The substitution of the very

rapid new methods for those already in vogue, requiring hours for precipitations and separations, which could be accomplished in a few minutes if accompanied by effective stirring, would perhaps recommend itself to the works chemist if this substitution could be made without the very considerable outlay now necessary for platinum electrodes. The very convenient Classen dish is not essential to the equipment requisite for electro-analysis, yet it is almost a necessity; one's equipment is scarcely complete without a number of them. To provide them, however, requires a considerable outlay.

By changing from the old system of electrochemical analysis to the new, a saving in the amount of platinum in use could undoubtedly be effected. The old system involves the use of the stationary, cylindrical, platinum cathodes, while the new methods depend on rotating electrodes, stirred solutions, the platinum dish and other devices for making possible the use of high current densities. The only points that can be produced in favor of the stationary electrode method is that the electrolysis can be started in the late afternoon and, without further attention, may be allowed to complete itself during the night, and that the multiplication of the number of analyses does not involve an equal increment in the time required for the operation. However, increasing the number of analyses does increase the number of electrodes which are necessary, and, therefore, increases the cost for equipment. With a single rotating anode and Classen dish cathode, a number of analyses could be made with a time expenditure of only a few minutes for each analysis and would require the attention of only a fairly expert chemist.

In equipping a new laboratory for electrochemical analysis, it is clearly poor economy to install the antiquated apparatus, the numerous stationary electrodes, in preference to the new, a much smaller number of rotating anodes and dish cathodes; and there are those who think, with reason, that it is also poor chemistry.

If our contention is true that it is both good economy and good analytical chemistry not only to equip laboratories with the apparatus requisite for performing rapid analyses in stirred solutions, but also, if necessary, to discard present equipment of stationary electrodes in order to do so, then much more true is our

contention if an apparatus constructed of a much less expensive material than platinum can be offered the profession.

Anticipating these advantages and encouraged by the success of the paraffined graphite electrodes, a graphite dish was prepared from a four-inch, cylindrical stick of Acheson graphite. This dish was turned out on a lathe by Mr. G. B. Upton, of Sibley College, Cornell University, for whose great kindness I take this opportunity of expressing my sincere appreciation.

Graphite was chosen as the material of which to construct the dish, because in it we have a substance which is at once a good conductor of the electric current, is cheap, is light in weight and is non-attackable by solutions. Its density is low, a little less than 2.2[1], but varies from one electrode to another, and in different parts of a single electrode. With the density probably also varies the hardness, though the variation in both density and hardness is slight and gradual, so no difficulty on that account need be experienced in machining. Because of its low density, the walls of a dish may be made of sufficient thickness to lend strength and rigidity to the article without unduly increasing its weight.

The porosity of the graphite may prove to be the greatest obstacle in the way of the dish becoming a success when employed in the most accurate analysis. The degree of porosity is expressed numerically as the quotient obtained by dividing the difference between the real and apparent specific gravities by the real specific gravity.[2] The apparent specific gravity is that obtained when interstices of the graphite are kept free of the liquid in which the determination is being made. This is accomplished by coating the sample lightly with shellac. The real specific gravity is found after the air has been removed from the pores of the sample by greatly reducing the pressure over the immersing liquid. When the suction is released the evacuated pores become filled. The average of several determinations gives the porosity of graphite at about 0.25. Such a degree of porosity would seem to make this substance an impossible one of which to construct a dish designed for such purposes as is this one. The paraffin, however, is very effective in preventing the absorption of solutions into the pores. That the latter are not entirely filled by the paraffin is shown by the fact that alcohol is able to

[1] FitzGerald, Trans. Am. Electrochem. Soc., **11** (1907).
[2] *Ibid.*

penetrate the paraffined graphite fairly readily. It is highly probable that while aqueous solutions do not enter the interstices, aqueous vapor does and condenses there to a certain extent; so it may be necessary eventually to fill these entirely with paraffin by the evacuation method used in the specific gravity determination.

The purity of graphite is high, and therefore it is improbable that any contamination of solutions can possibly result from its use. It has been shown[3] that when a carbonaceous substance, like anthracite coal, has been graphitized, its impurities are almost completely volatilized, the more complete being this volatilization the higher the temperature of graphitization and the longer the heat is maintained. This graphite is then a very pure form of carbon, and the Acheson product, in addition to its insolubility, has been shown[4] to be very resistent to disintegration in solution. When made anode in caustic solutions it is only very slightly attacked by the evolved oxygen. This is to be expected when we recall that the combustion point of some forms of graphite in oxygen is about 600° C.

Graphite is to be had of varying degrees of hardness, the harder varieties, while less pure, are more resistent to chemical action and undoubtedly would make a stronger and more durable article. Hardness would likewise enhance the possibilities for accurate and sharp machining, a fact to be borne in mind when choosing a graphite for the purpose described in this paper.

Its tensile strength is about 80 per cent. of that of the carbon from which it is made, there being a deterioration of 20 per cent. in that property during the process of manufacture. With the combination of hardness and the above tensile strength, it is possible to machine a dish whose walls are of very slight and uniform thickness, which thus possesses both strength and lightness. The elasticity of the harder varieties of graphite is also worthy of note. Possessing these properties, there is no reason why a graphite dish with proper use should not prove to be long-lived to an entirely satisfactory extent.

The experimental dish was prepared for use by first burnishing on a revolving, steel-wire buffer, which served to remove all dust and gave the surface a somewhat polished appearance. The

[3] FitzGerald, Jr., Frank. Inst., Nov., 1902.
[4] Foerster, Zt Ang. Chem., June, 1901.

graphite still rubbed off on the fingers, but to a much lessened extent; after treating with paraffin it no longer rubbed off at all.

The dish was warmed in a hot-air bath to a temperature of about 110°, and, while still hot, molten paraffin was applied with a brush until it was no longer absorbed readily, but remained visible on the surface. The dish was then returned to the oven, several sheets of filter paper were placed under it and the bath was maintained at the temperature of 110° for several hours. In this way the excess of paraffin was drawn off, by gravity and capillary action, into the filter paper. After this treatment the surface of the graphite appeared quite dry. The dish was then reburnished.

The preliminary experiments conducted with this dish gave such very promising results that two other dishes were obtained through the courtesy of Messrs. Eimer and Amend, of New York. These are much lighter in weight, weighing, respectively, 38 and 32 grams after having been paraffined. Their capacity is 200 c.c. In dimensions they are 9.5 cm. in diameter across the top and are 5 cm. deep. The lower part has the shape of a truncated cone, the conical shape beginning 2.5 cm. from the upper edge and extending inward at such an angle that a flat bottom of 3.5 cm. in diameter is afforded by the truncation. This shape was chosen so as to give a dish of straight sides. The walls are slightly less than 1 mm. in thickness. The interior of the dishes presents a surface area of 54 square centimeters.

Another dish has been designed which is hemispherical in shape, with the exception of a flattened portion of 3 cm. diameter on its bottom. Its dimensions are 9.5 cm. in diameter across the top and 4.5 cm. deep. The hemispherical shape has the advantage of affording the greatest capacity for the least wall area. As, of course, the weight of the dish lies in its walls, the smaller the area of the walls the less will be the weight. The hemispherical dish therefore gives the greatest capacity for the least weight.

The first experiments were made to determine the most satisfactory method for drying, attention being paid to speed as well as to accuracy. A method frequently used in drying the Classen dish with deposited metal is to wash with absolute alcohol and to burn off the excess. Applying the severest test first, this method

of drying was used; the dishes were washed with distilled water, followed by absolute alcohol and the excess of alcohol was burnt off. After cooling in a desiccator the dishes were weighed.

Some of the results showed only a slight loss in weight, while others showed a loss of almost 5 mg., due, no doubt, as was found, to the loss in paraffin through being dissolved by the alcohol.

The method was then adopted of drying, after washing with distilled water, by holding the dishes by means of crucible tongs directly over the smokeless flame of a Bunsen burner, moving then around during the drying so that the heating would be uniform, and then cooling in a desiccator. This extremely crude method was justified by its rapidity and the surprisingly satisfactory results, as is shown by Table I.

TABLE I.

No.	Weight Before: Grams	Weight After: Grams	Loss: Grams
1	37.2660	37.2660	None
2	37.2660	37.2658	0.0002
3	37.2658	37.2652	0.0006
4	33.1400	33.1400	None
5	33.1400	33.1400	"
6	33.1400	33.1400	"

A number of determinations of efficiency was then made by electrolyzing an acidified solution of copper sulphate contained in a graphite dish in series with a copper coulometer filled with a portion of the same solution. Copper anodes were employed in both cells and a copper cathode in the coulometer. A current of 0.1 — 0.16 amperes was passed and the electrolysis was continued for about one hour in each run. Some of the results obtained are given in Table II.

TABLE II.

No.	Cathode Gain in Coulometer: Gram.	Cathode Gain in Graphite Dish: Gram.	Difference: Gram.
1	0.1140	0.1128	—0.0012
2	0.1582	0.1570	—0.0012
3	0.1784	0.1770	—0.0014
4	0.1748	0.1728	—0.0020
5	0.2008	0.2004	—0.0004
6	0.1924	0.1920	—0.0004
7	0.1924	0.1924	—0.0000
8	0.1772	0.1758	—0.0014
9	0.1818	0.1802	—0.0016
10	0.2126	0.2122	—0.0004

An occasional result failed signally to agree with the theoretical value. As a check on the method, a Classen dish, containing a similar solution and copper anode, was also placed in the circuit; this cell was worked in series with the other two. The platinum dish was dried with alcohol, the excess of which was burnt off, and was cooled in a desiccator. The results gotten with the Classen dish are shown in Table III.

TABLE III.

No.	Cathode Gain in Coulometer: Gram.	Cathode Gain in Classen Dish Gram.	Difference: Gram.
1	0.1140	0.1142	+0.0002
2	0.1084	0.1040	—0.0044
3	0.1748	0.1768	+0.0020
4	0.2008	0.2030	+0.0022
5	0.1924	0.1919	—0.0005
6	0.1772	0.1753	—0.0019
7	0.1818	0.1807	—0.0011

These results, as a whole, are hardly as good as those obtained with the graphite dish and, like those, an occasional one was bad. The errors observed in the case of the Classen dish are doubtless due to hurried and perhaps careless manipulation. It may be noticed, moreover, that in the case of the graphite dish the results are mostly low, while in that of the platinum they are sometimes high and sometimes low.

In Table IV, the results obtained with the Classen dish are tabulated against those obtained with the graphite dish.

TABLE IV.

No.	Cathode Gain in Platinum Dish: Gram.	Cathode Gain in Graphite Dish: Gram.	Difference: Gram.
1	0.1142	0.1128	—0.0014
2	0.1040	0.1038	—0.0002
3	0.1650	0.1642	—0.0008
4	0.1768	0.1728	—0.0040
5	0.2030	0.2031	+0.0001
6	0.1919	0.1920	+0.0001
7	0.1997	0.1974	—0.0023
8	0.1753	0.1758	—0.0005
9	0.1807	0.1802	—0.0005
10	0.2125	0.2122	—0.0003

The results obtained for the graphite dish, as set forth in this table, are for the most part likewise lower than those obtained with the platinum dish. It appears that there is perhaps some

loss in the weight of the dish itself in drying, which causes the low results. Therefore, the method of drying directly over the flame will be abandoned and, instead, the dishes will be washed thoroughly with distilled water and then dried rapidly in a stream of warm, dry air.

The dishes are now being tested in actual analytical work. Known volumes of a standard copper solution are being analyzed in them with rotating anode and at high current density. This will be considered a crucial test, and not until the results of this test are known can the dish be unqualifiedly recommended. This paper is, therefore, merely a preliminary note. No further tests are needed, however, we feel, to show that it may be substituted profitably in numerous electrochemical operations where the Classen dish has been employed heretofore, or would have been had it been a less expensive article.

These dishes have been suggested for use in other operations not connected with electrolysis, such as digestions in hydrofluoric acid at high temperatures. In such cases the beaker shape would probably be advantageous.

A rotating graphite anode has been designed to accompany the dishes. This is constructed after the general plan of the platinum anode described by Miss Langness.[5] It is dish-shaped and contains radial slits in its walls and a circular opening in its bottom. It is hoped that by means of it the interesting results obtained with the anode referred to above may be duplicated.

Work is now being carried on, as intimated above, to show the limiting capabilities of the graphite cathode dish.[6] A further report, therefore, will be made. The efficacy of the dish in numerous electrochemical separations and operations will also be determined. It is also our intention to investigate the rotating dish anode referred to above and a smaller, disc-shaped, rotating anode with a graphite stem.

Summary.

1. Simple graphite electrodes are described which are designed for use in the place of platinum as insoluble electrodes in electrochemical experiments.

[5] J. Am. Chem. Soc., **29**, 459 (1907).

[6] Manufactured and on sale by Eimer & Amend, New York.

2. An account is given of preliminary experiments with a graphite dish intended to supplant in some forms of electrochemical analysis the Classen platinum-dish.

3. The dish is recommended for electrochemical separations and for analyses where great accuracy is not required. Confidence is felt that, after it has been further developed, it will be able to entirely take the place of the platinum cathode dish.

Wesleyan University, April 1, 1909.

DISCUSSION.

Prof. H. K. Richardson (*Communicated*): The treatment of the dish could, I believe, be improved by the following process: First, boil it one hour in paraffin, held at 150° C.; second, heat the dish so boiled one hour at 250° C. (a baking-out process). This treatment will drive out excess of paraffin. Carbons treated as above do not lose weight when heated to 175° C., also gasoline or alcohol seem to have little effect upon them, thus making it possible to burn off a dish so treated in the usual manner. I offer this suggestion for what it is worth, and hope it may work out in this case the same as it has done in work with carbons.

A paper presented at the Fifteenth General Meeting of the American Electrochemical Society, at Niagara Falls, Canada, May 8, 1909; President E. G. Acheson in the Chair.

A MODIFIED OXY-HYDROGEN GAS COULOMETER.

By J. W. Turrentine.

In taking measurements of quantity of electricity, two methods may be chosen,—either the determination of current strength through the duration of a definite time interval, the product of amperes into time, giving the number of coulombs, or the determination of the coulombs directly by means of the decomposition products liberated, in accordance with Faraday's second law, from an electrolyte by the current.

The first method requires the frequent reading of current strength, since this is liable to fluctuations, and frequent readings are necessary in order to obtain a reliable average.

The second method is much to be preferred, as only the final amount of the accumulated decomposition products is determined, so that the constant attention of the operator is not required.

The cell in which the electrolytically induced decomposition products are formed, and the adjoined apparatus for accumulating them, is styled a *coulometer,* from the fact that it is employed in measuring coulombs, the name being an abbreviation of *coulombmeter.* This term is not a new one, though, unfortunately, it has not yet come into general use in electrochemical literature. It was first suggested by Prof. T. W. Richards, of Harvard University, as a substitute for the name voltameter, previously employed, the object being to obviate the confusion existing between the names *voltameter* and *volt-meter.*

The measurement of the coulombs, however, is not always the ultimate object of the use of the coulometer, but more frequently the determination of the current efficiency in some cell run in series with the coulometer is desired. The electrode products in the coulometer, which are measured, should then represent 100

per cent. efficiency. The electrode reactions must, therefore, be simple ones and must take place quantitatively.

The fact that in some coulometers the product to be measured is metallic and in others is gaseous gives us a simple method of classification. Of the former sort, the silver and copper coulometers are in most general use, while of the latter, the oxy-hydrogen gas coulometers are universally employed. Expediency determines these forms, as they are the simplest.

When its use is possible, the gas coulometer is preferable, since the determination of the amount of the evolved gases may be made directly, either by weighing the cell before and after the electrolysis, as in runs of long duration, or by reading directly the volume of the evolved and accumulated gases. This obviates

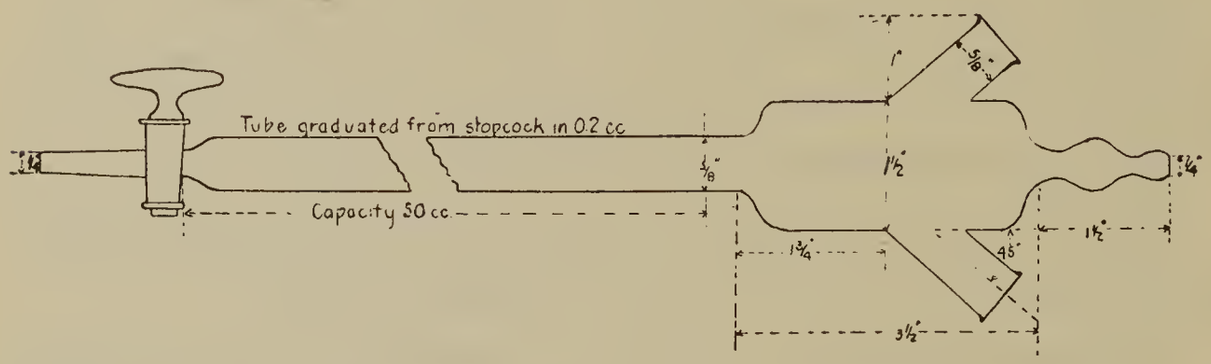


FIG. 1.

the inconvenience of drying and otherwise preparing the deposited metal for weighing. Where very small measurements are to be made, the gas coulometer is not only more convenient, but also more accurate, as the gas volumes can be read with much greater accuracy than a slight metal plate can be weighed. While one coulomb causes the deposition of only 1.118 milligrams of silver and 0.3294 milligrams of copper, it liberates 0.12 c.c. of hydrogen. The gases liberated in the gas coulometers are either (*a*) allowed to escape through a depth of fused calcium chloride or other desiccating agent to dry them, the loss in weight of the cell representing the weight of the evolved gases, or (*b*) they are conducted from the cell into a eudiometer, where they are measured, or (c) they are allowed to collect in the anode and cathode compartments of the coulometer respectively, and the volume of the oxygen and hydrogen are then read separately,

or (*d*) they are allowed to pass together into a single, graduated tube, where their aggregate volume may be read.

The first type of gas coulometer here mentioned (*a*), used only in runs of long duration and when the loss in weight due to the evolved gases is quite appreciable, may be called the *weight* gas coulometer.

The second type (*b*) is quite undesirable because measurements made by means of it involve corrections for the downward pressure of the undisplaced liquid column in the eudiometer.

The same criticism also applies to many of the so-called two-arm coulometers (*c*), as this form is rarely supplied with a leveling bulb and the gas volumes consequently must be reduced to atmospheric pressure by correcting for the weight of the confining liquid columns.

The most convenient type (*d*), is represented by the Walter-

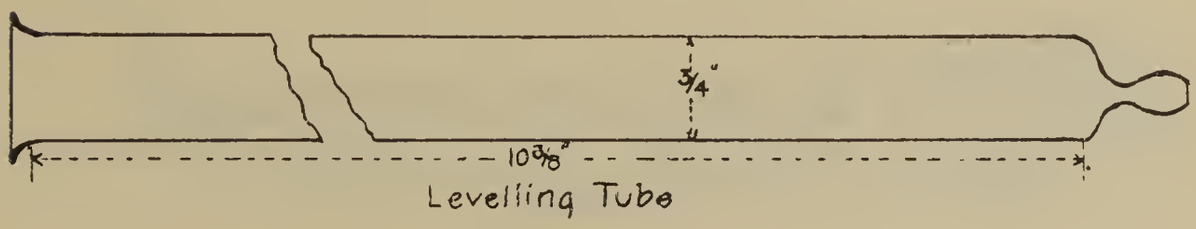


FIG. 2.

Neumann single tube coulometer. This is provided with a leveling bulb, and therefore becomes a direct reading instrument. This form is especially convenient for all current efficiency experiments when the electrode products are wholly, or in part, gaseous. The leveling bulb makes it possible to read the gas volumes which are to be compared, at atmospheric pressure.

The Walter-Neumann coulometer is constructed of a single, upright tube, graduated, with an oblong, bulbous enlargement at its lower end, containing the electrodes, and is surmounted on its upper end by a stop-cock and capillary tube. The lower end is joined by means of a length of rubber tubing to a leveling bulb. The electrodes are corrugated plates of platinum foil mounted on thin platinum wires, the latter being sealed through the walls of the bulb and terminated on the outside in small, tight coils, or loops. Electrical connection is made with the electrodes by hooking wires in these external loops.

The disadvantages of the apparatus are due to the fragility of the terminal wires and the glass seal which holds them. The platinum terminal wires, being thin, are easily bent, and, in spite of care, are soon broken off. This renders the apparatus useless. Further, only poor contact is gotten with the terminal loops by hooking wires in them, yet this is the only means that may be employed for completing the electrical connection. If wires are fastened more securely in the coils, the latter are almost immediately broken off. The poor connections, with resulting imperfect contacts, lead to local heating. The heat is conducted to the glass at the seal, which expands. Alternate expansion and contraction causes the glass to crack and the tube to leak. This also renders the apparatus useless. When the tube is thus put out of commission the electrodes, perhaps the most expansive part of the apparatus, must be scrapped. These

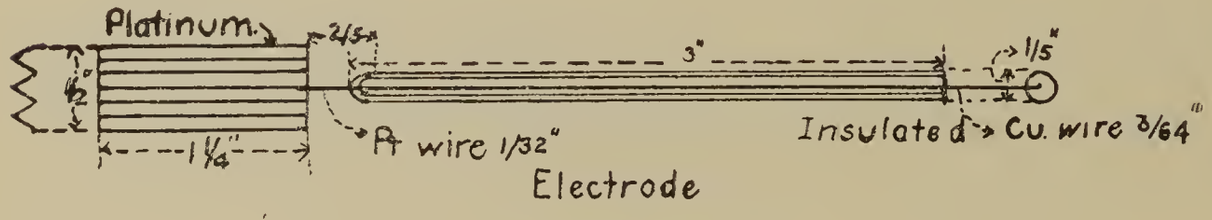


FIG. 3.

objections, while few, are so serious that they render the apparatus entirely impracticable for frequent use.

The Walter-Neumann apparatus has been modified in such a way that these objectionable features have been obviated. While the same general shape of the older apparatus has been retained, the upright tube has been slightly narrowed to about five-eighths inch in diameter and lengthened, thus giving somewhat more accurate readings, and the graduations have been extended to 50 c.c., from 40 c.c., in the old apparatus, thus increasing the capacity. The graduations, in 0.2 c.c., are made from the stop-cock downward. Above the stop-cock extends a short capillary tube, through which connection may be made with a gas burette should an analysis of the coulometer gases be desired.

The lower, bulbous portion of the main tube has been greatly changed. This bulb is oblong and is 3½ inches in length by 1½ inches in diameter. Instead of the two platinum wires, it

now carries, sealed in its walls, two side arms, or tubes, opposite each other and at an angle of 45° to the perpendicular, or longitudinal, axis of the tube. They are made to slope downward at this angle, so that gas bubbles, carried into them by convection currents, can not become lodged. The side arms are five-eighths inch in diameter; they enter the bulb at a point 1¾ inches from its upper extremity and extend one inch outward, measured perpendicularly from the lateral walls of the bulb.

The electrode plates are made of thin platinum foil and are deeply corrugated to enlarge their surface. They are 1¼ by ½ inch in dimensions and afford an electrode surface of at least a square inch on each face. Supporting them is a short section of platinum wire, which is sealed in a length of glass tubing of one-fifth inch external diameter and three inches long, and which

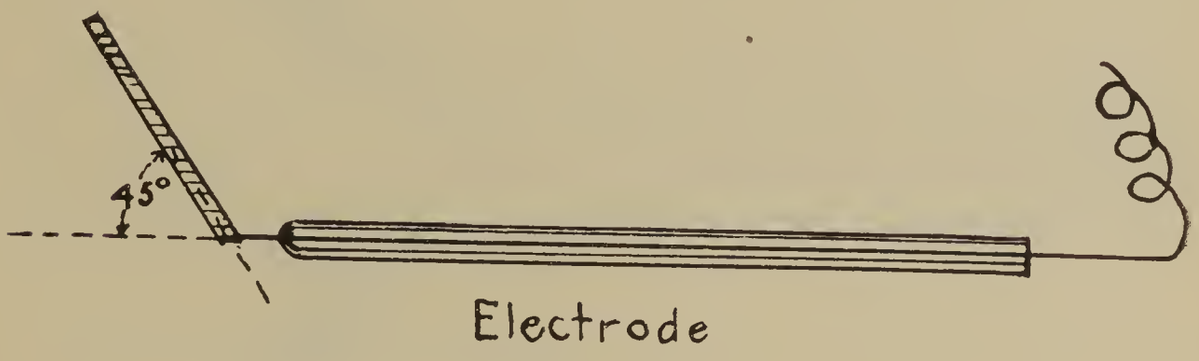


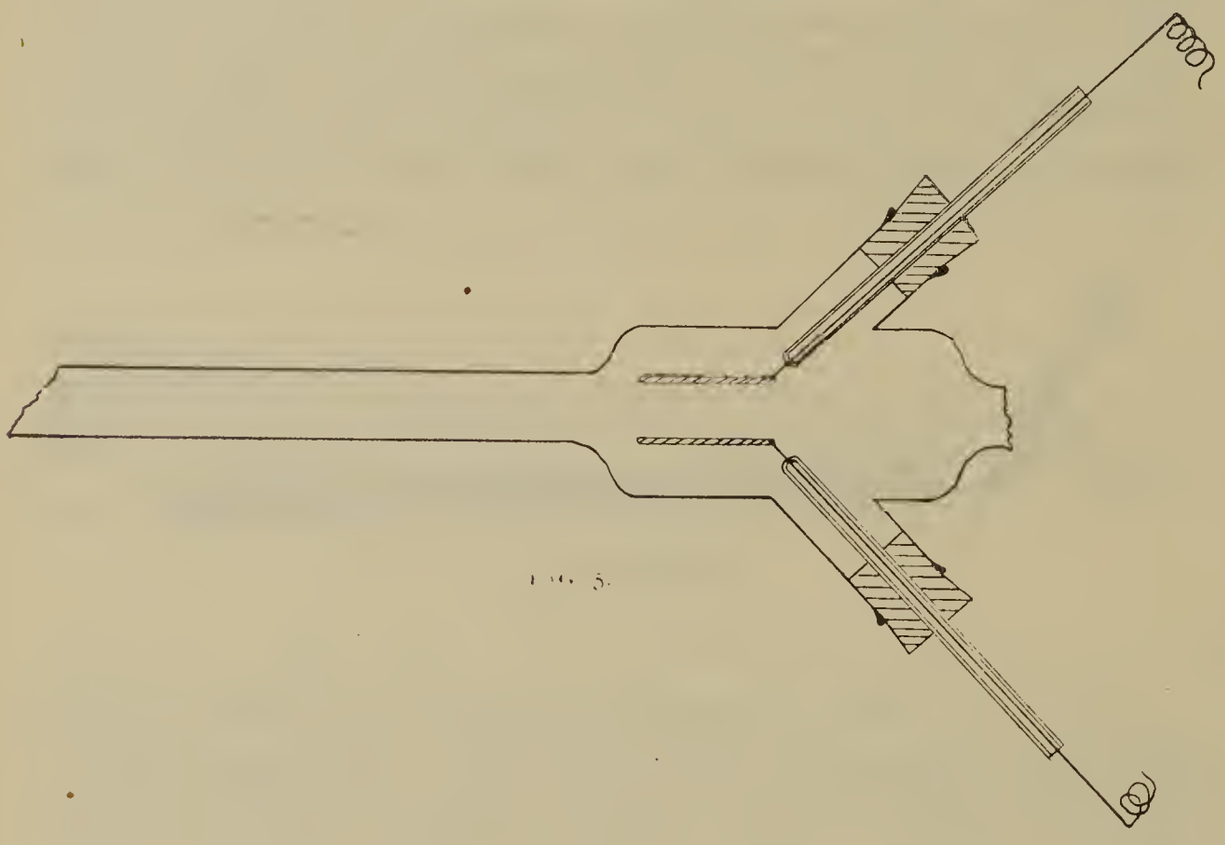
FIG. 4.

is welded to a piece of insulated copper wire about a foot in length and extending through the tube. The glass tubes are inserted through one-holed rubber stoppers, which fit the side arms.

The plane of the electrode plates makes an angle of 135° with the longitudinal axis of the glass tubes by which they are supported. These tubes, when in place in the coulometer, are, of course, parallel with the side arms through which they project. The side arms, being at an angle of 45° to the coulometer tube, and the electrode plates being at an angle of 135° to the side arms, the plates, when placed in position in the coulometer, are parallel to the coulometer tube and to each other. They thus face each other in a vertical position. By pushing the glass through the stoppers, the electrodes may be brought closer together or farther apart, as desired.

This construction renders the electrode easily detachable. This is especially desirable when they need cleaning.

In case the glass parts are broken, the electrodes may be removed and placed in a new tube. This requires the purchasing of glass parts only after the initial acquirement of the electrodes. The length of copper wire is sufficient to furnish an elastic coil and to fasten to the external circuit by means of screw connectors. Thus perfect electrical contact is assured and local heating is avoided. Should breaks in the glass seals occur they



may be readily mended. As the electrodes are not subjected to very much wear, they should be quite long-lived.

The glass in the ends of the side tubes is thickened so that, if desired, the rubber stoppers may be wired in. This, however, experience has shown, is entirely unnecessary for ordinary solutions, as the friction of the rubber against the glass is quite sufficient to hold them firmly in place. When this friction is lessened by solutions of such substances as caustic soda it may be necessary at times to fasten the stoppers more securely.

The bulb of the coulometer below the side arms is drawn out, through a length of 1½ inches, into a constricted portion whose

walls are undulatory in outline. It terminates in an opening a quarter of an inch in diameter. Over this opening fits the end of a section of rubber tubing, which joins the coulometer tube with the leveling tube. The uneven walls of the constricted portion serve to hold the rubber tube in place.

For the leveling bulb employed in the old apparatus is substituted in the new one a leveling tube. Its advantages are that it is more easily handled and admits of a more accurate and rapid reading of the levels in the two parts of the apparatus. The leveling tube exceeds in capacity that of the graduated portion of the coulometer tube. It is about 11 inches in length and has an internal diameter of three-quarter inch.

The apparatus may be readily supported in ordinary burette clamps or iron stands, with which all laboratories are provided. Special stands, while they may be obtained and are convenient, are not at all necessary.

While the disadvantages of the Walter-Neumann coulometer have been overcome, at the same time, as has been abundantly evidenced by the specimens[1] in use in the laboratory, the modified form does not suffer in comparison in point of compactness and neatness of appearance.

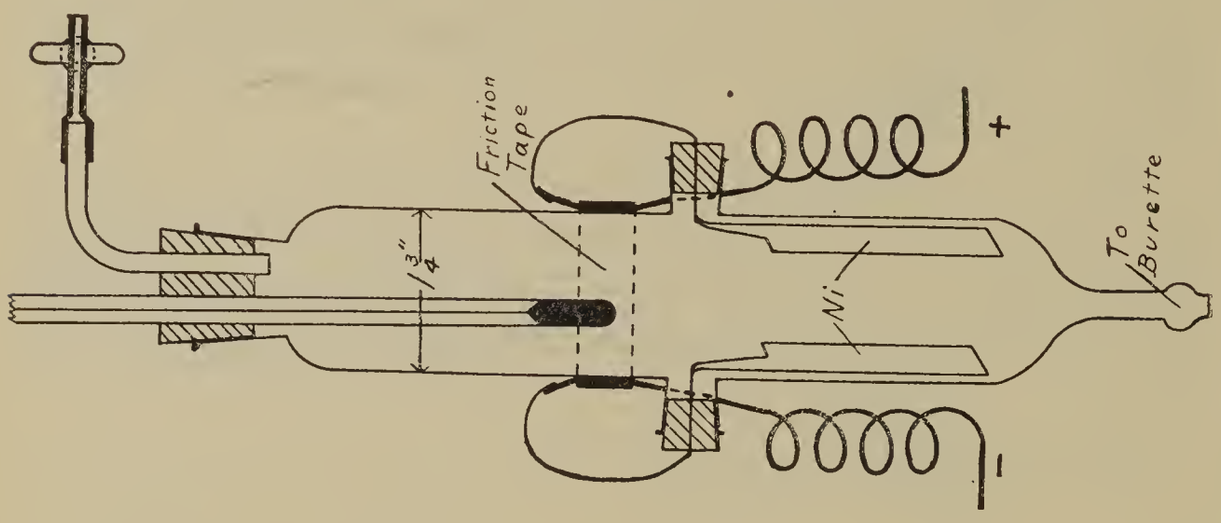
Electrochemical Laboratory,
Cornell University.

DISCUSSION.

MR. F. C. FRARY (*Communicated*): It seems to me that the apparatus described could be further simplified by omitting the graduated tube with its glass stop-cock and inserting in its place a tubulure carrying a rubber cork. Through the cork pass a thermometer and a delivery tube, the latter normally closed by capillary rubber tubing and pinch-cock. For a leveling tube, a 25, 50, 100 or 200 c.c. burette is used. The 1.5-inch tube is made longer and an air space left above the liquid. Starting the apparatus with the level of the liquid in the burette and main tube the same, the increase in volume is read off on the burette

[1] Manufactured by Eimer & Amend, who have the drawings and specifications.

at the close of the experiment by lowering it until the gas is again under atmospheric pressure. If the upper tubulure has a diameter of about an inch, electrodes of that width may be used, while in the apparatus described the electrodes can not be more than half an inch wide. This modification also permits the side-arms to be set perpendicularly to the main body if the glass tubes carrying the electrodes are shortened, and the whole can easily be made from a broken condenser-jacket by any one with a moderate knowledge of glass-blowing. The extra expense of the specially graduated part and the stop-cock is avoided, and the use of ordinary burettes (without stop-cocks) allows widely varying volumes to be measured with the same percentage



error. The accompanying diagram shows this apparatus as it has been used in the electrochemical laboratory of the University of Minnesota for the past two years. For large currents (3/8 amperes) nickel electrodes are used, as shown in the diagram, and the electrolyte is 15 per cent. NaOH (free from chlorine). For small currents platinum electrodes are better, as shown by Riesenfeld.[1] With nickel electrodes the glass tube carrying the electrodes is omitted and a thin strip of the electrode material brought out through the cork and soldered to a copper wire as shown. The volume of the gas must, of course, be corrected for the vapor-tension of the electrolyte over which it is collected. The use of the burette for a leveling tube is not claimed as original, but the form of the main cell seems to be new, and somewhat simpler than the form described in the preceding paper.

[1] Z. Electrochem. (1906), **12**, 621.

A paper presented at the Fifteenth General Meeting of the American Electrochemical Society, at Niagara Falls, Canada, May 7, 1909; President E. G. Acheson in the Chair.

THE ELECTROLYTIC DEPOSITION OF PLATINUM.*

By W. J. McCaughey.

Platinum is deposited on a copper or brass bar as a bright, shining deposit merely by immersing the bar in a solution of chlorplatinate of potassium. This deposit, however, is not of great depth nor is it adherent, since its deposition is entirely dependent upon the chemical replacement in solution of platinum by the copper and zinc of the brass. This dissolution of the zinc and copper is more or less uneven and leaves the surface upon which the platinum is deposited porous, therefore the contact is not intimate enough to insure an adherent deposit. In order to secure a good surface upon which to deposit the platinum, this tendency of the brass to dissolve in the electrolyte must be overcome.

Deposition of platinum, and accordingly solution of the brass, takes place much more readily in acid solution than in a neutral solution or in one made slightly alkaline with NaOH. The deposition of platinum by brass from a hot solution is almost instantaneous. In order to overcome the solution tendency of the copper and zinc, and to plate the platinum directly on the brass, the circuit is completed by immersing the brass cathode in the hot saturated solution of potassium chlorplatinate. When the cathode (article to be plated) is the vessel containing the electrolyte, the position of the anode is carefully adjusted and the circuit completed by pouring in the hot electrolyte. By these means a reducing environment is established around the article to be plated, thus overcoming in part at least, the solution of the brass, and effectually preventing pitting on the surface of the brass.

The primary object of this work was to secure a set of platinum plated bottles in which to carry on solution studies.

To render the bottles perfectly secure against solution of their

* Published by permission of the Secretary of Agriculture.

own material during plating, they were given a deposit of gold from an alkaline cyanide solution. The gold deposited, though soft, is adherent and offers an excellent surface upon which to build the harder deposits of platinum.

Difficulty was met in depositing platinum from hot concentrated potassium chlorplatinate solution. On electrolysis the solution near the cathode becomes alkaline, and after ten to fifteen seconds as the concentration of KOH increases there is formed a dark cloud of finely divided platinum. Evidently this is due to the reduction of platinum from its salts—alkaline solution being most favorable for the reaction. This cloud spreads rapidly through the electrolyte, and must be removed by filtration to insure an adherent deposit of platinum upon the cathode, otherwise the platinum coating is crusty. But with stationary electrodes this cloud of fine platinum is soon formed again, thus rendering it practically impossible to secure a deposit of the metal under these conditions. When the anode is rotated, stirring the solution, the formation of this cloud is delayed and a fair deposit obtained. Addition of a little hydrochloric acid also checks the formation of the fine platinum cloud.

To take care of this reduction it is necessary to remove the causes:

1. Removal of reducing hydrogen.
   - (*a*) Reduction of current density.
   - (*b*) Chemical means.
2. Prevention of alkaline environment.
   - (*a*) Acidification.
   - (*b*) Use of $(NH_4)_2PtCl_6$.
   - (*c*) Rotation of electrode.

Preliminary experiments were made with solutions of platinum hydroxide in phosphoric and in oxalic acids with negative results. Potassium chlorplatinate and cyanide solution of potassium chlorplatinate were also used. The deposit from a cyanide solution was very good, but after a time the platinum in solution formed complex cyanides from which it was impossible to precipitate metallic platinum by the current.

The electrolyte formed by addition of citric acid to a saturated solution of potassium chlorplatinate gave the best results, consequently it was thought best to confine our attention to this

electrolyte. Various quantities of citric acid were tried, and in general it was found expedient to use a solution of the following concentration:

2.0 grs. potassium chlorplatinate.
10.0 " citric acid.
100 c.c. water.

This high proportion of citric acid favors the formation of a better deposit. The platinum content of the solution may be renewed as it becomes exhausted, but finally the solution ceases to give a smooth deposit. Citric acid does away in part with the formation of a platinum cloud around the cathode. With continued use, however, it seems to lose its efficiency. One cubic centimeter of hydrochloric acid revives it again by correcting the alkaline environment formed at the cathode. The presence of free mineral acid, however, is not desirable, particularly if plating directly upon copper. With ammonium platinic chloride the addition of hydrochloric acid was not found necessary, and the deposit was as good as that obtained from the potassium salt.

The use of a rotating anode delays the formation of an alkaline cathode environment, and gives a good deposit of platinum from hot concentrated potassium chlorplatinate solution. However, in the internal plating of bottles, the centering of the anode must be very exact to secure even distribution of the current; this is impracticable with a rotating anode, consequently this method was not used.

When the current is diminished so that there is no liberation of hydrogen at the cathode, platinum is deposited in a bright, polished silver-like coat. Beautiful as this deposit is, it is not adherent save in thin layers. When we attempt to build upon it, it peels in the subsequent buffing and scratch brushing. This peeling generally begins at the edges or sharp corners and extends all over the deposit.

The deposition of the bright shining deposit or of the hard steely deposit depends upon the current density; low current density gives the non-adherent platinum.

The influence of the current density upon the nature of the deposit is clearly demonstrated in plating the lids of the bottles. Owing to the irregular shape of the lid (Fig. 1) we have the cur-

rent density varying greatly. The bottom and sides of the lid were plated with the black adherent deposit, while the tops and angles between the sides where the current density was small, were plated with the bright non-adherent coat. Deposition along the upper part of cylindrical sides *B* of the lid was difficult on account of the uneven distribution of the current and the consequent low current density. The uneven current distribution effect was also observed on the cylindrical body of the brass bottle. The placing of the anode is a very important detail of the process. Where the anode was placed too high the sides show the steely deposit while the bottom is covered with the brilliant plat-

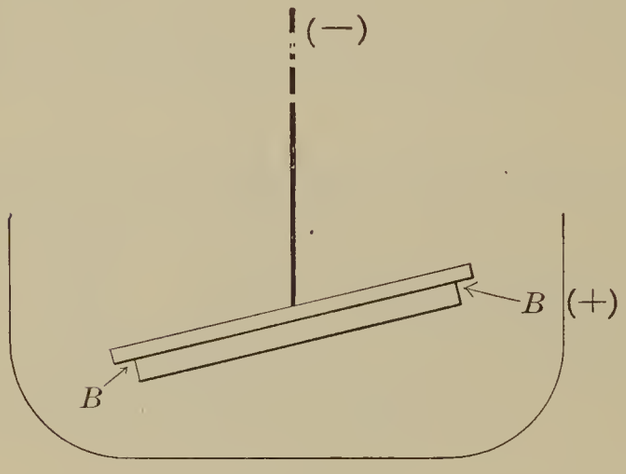


FIG. 1.

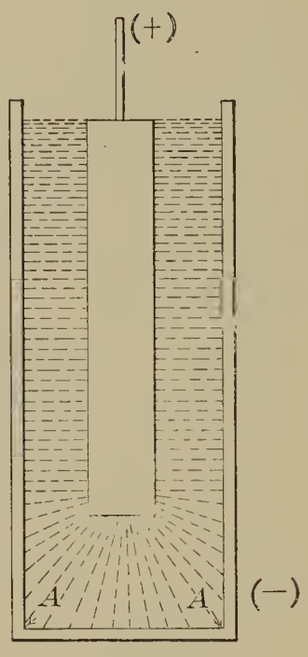


FIG. 2.

inum. Difficulty was experienced in depositing the dark platinum in the remote angles of the bottle.—*A* Fig. 2.

In bottle No. 4 where the adjustment of the anode was favorable, the dark steely deposit was obtained all over the interior of the bottle except in the edges where the drop in current density caused deposition of brilliant platinum. This is a serious fault, for the line of demarcation between the steely deposit and the bright metallic deposit is clearly apparent; and on buffing the peeling starts at the edge between the sides of the lid and the thinly plated top.

The total area of the inside surface of the bottle was 220 square centimeters. A current of 0.25 ampere was used to secure the

best deposit. This corresponds to some 0.114 ampere per square decimeter, or about one ampere per square foot. The lids were 51.2 square centimeters in area; the current, 0.10 ampere; the current density, 0.193 ampere per square decimeter, or about 1.8 amperes per square foot. The formation of the hard crusty deposit of platinum at this high current density was avoided by keeping the lids in the plating bath only a short time, usually about one minute. The thick deposit was obtained by repeated treatment with fresh solution.

The same difference in the deposited metal is noticed by varying the current strength. With a current of a quarter of an ampere the deposit on the cylinders is of the steely variety. By increasing the current to 0.5 ampere and rotating the anode, a very good deposit was obtained, but this deposit at 0.5 ampere is hard and likely to be crystalline. This hard crystalline deposit, in buffing, causes much trouble, as it is so hard that it cuts away the previously deposited platinum metal and scratches the inside of cylinder.

Effect of concentration: By increasing the concentration of the chlorplatinate to saturation in hot solution these hard crystals of platinum were deposited on the inside of the bottle, using a current of 0.25 ampere.

Evidently there are limiting conditions of current density, of concentration and of acidity which determine the character of the platinum deposit.

Bureau of Soils,
U. S. Department of Agriculture,
Washington, D. C.

A paper presented at the Fifteenth General Meeting of the American Electrochemical Society, at Niagara Falls, Canada, May 7, 1909; President E. G. Acheson in the Chair.

ELECTRO-DEPOSITION OF SOME METALS FROM ACETONE SOLUTION.

By Harrison E. Patten and William Roy Mott.

Continuing our previous work[1] on the electrolysis of metallic salts dissolved in non-aqueous solvents, the following experiments were carried out. Saturated solutions in acetone were made, using as solutes NaI, SrI_2, $CdCl_2$, $FeCl_3$, $CuCl_2$, $SnCl_2$, $SbCl_3$ and $BiCl_3$. These were electrolyzed between platinum electrodes to ascertain whether the metal would deposit or not; and if so, at what current density and cathode polarization. Similarly a solution of $AsCl_3$ in acetone, about 10 per cent. by volume, was electrolyzed and a good deposit of arsenic secured, but the cathode and anode discharge potentials were not obtained owing to interruption of the work.

The general methods used for determining the decomposition voltage, anode and cathode polarization and discharge potentials, have been given in our former papers.[2] Table I contains a summary of the results of the present investigation.

Smooth deposits of cadmium, tin, antimony, bismuth and arsenic were obtained at low current densities, the tin showing a marked tendency to tree at higher current densities. The deposits have not been tested for adherence, behavior under

[1] Single Potentials of Zinc in Aqueous Solutions, Trans. Am. Elect.-Chem. Soc. **3**, 317 (1903); Experimental Determinations of the Single Potentials of the Alkali Metals, Sodium and Potassium, Electrochemical Industry, September, 1903; Decomposition Curves of Lithium Chloride and the Electro-deposition of Lithium, Jour. Phys. Chem. 8, 153 (1904); On the Deposition of Zinc from Zinc Chloride Dissolved in Acetone, Ibid. 8, 483 (1904); An Analytical Study on the Deposition of Aluminum from Ethyl Bromide Solution, Ibid. 8, 548 (1904); The Deposition of Metallic Calcium from Alcoholic Solutions, Electrochem. Industry **1**, 418 (1903); The Deposition of Sodium from a Solution of Sodium Iodide in Acetone, Ibid. **1**, 418 (1903); The Electrolytic Reduction of Nitric Acid, Trans Am. Electrochem. Soc. **12**, 325 (1907); Decomposition Curves of Lithium Chloride in Acetone: the Effect of Water, Jour. Phys. Chem. **12**, 49 (1908); Single Potentials of the Halogen Elements, Trans. Am. Electrochem. Soc. **5**, 73 (1904); On the Heat of Solution of Aluminum Bromide in Ethyl Bromide, Trans. Am. Electrochem. Soc. **7**, 177 (1905).

[2] Potentials of Zinc in Aqueous Solutions; Decomposition Voltage of Lithium in Alcohols and the Electro-deposition of Lithium; Electro-deposition of Lithium from Pyridine and from Acetone; the role of Water.

buffing, or for carbon content, as this paper is essentially a preliminary survey. The deposition of sodium[3] and of strontium is interesting, as we were able to secure a cathode polarization

TABLE I.

Summary of Data on Electrolysis of Metallic Chlorides and Iodides in Acetone Between Platinum Electrodes.

Current Density Amperes per Sq. cm.	Polarization of Cell: Anode Volts	Polarization of Cell: Cathode Volts	Polarization of Cell: Total Volts	Temp. °C	Solute	Remarks
0.100	—0.70	+1.10	+1.7	28	Na I	
0.100	—1.10	+1.10	+2.20	. . . .	Na I	
0.200	—0.90	+2.20[D]	+3.1	26	Na I	Na deposited.
0.1	—0.70	+0.50[D]	+1.1	28	$Sr I_2$	
0.2	—0.70	+2.20[D]	+2.90	28	$Sr I_2$	Sr deposited.
0.001	—1.79	—0.12	+1.5	. . . .	$Cd Cl_2$	Cd deposited.
0.000	—0.751	—0.751	+0.00	27	$Fe Cl_3$	
0.010	—0.85	—0.75	+0.3 (?)	. . . .	$Fe Cl_3$	
0.060	—1.10	—0.40	+0.40	. . . .	$Fe Cl_3$	
0.200	—1.17[D]	—0.06[D]	+1.20(?) +1.50	. . . .	$Fe Cl_3$	Fe deposited.
0.000	—0.90	—0.90	0.00	. . . .	$Cu Cl_2$	
0.100	—1.06[D]	—0.04[D]	+1.02	. . . .	$Cu Cl_2$	Cu deposited.
0.001	—1.00	—0.18	+0.8	. . . .	$Sn Cl_2$	Sn deposited.
0.010	—3.10	—0.18	+2.9	26	$Sn Cl_2$	
0.100	—3.60	—0.18	+3.3	. . . .	$Sn Cl_2$	Sn trees.
0.010	. . . .	. . . .	+2.8	. . . .	$Sn Cl_2$	
0.100	. . . .	. . . .	+3.6	. . . .	$Sn Cl_2$	Sn trees.
0.0007	—1.98	—0.22[D]	. . . .	22	$Sb Cl_3$	Sb deposited.
0.0013	—2.05	—0.22[D]	. . . .	. . . .	$Sb Cl_3$	
0.0023	—2.01	—0.27	. . . .	. . . .	$Sb Cl_3$	
0.028	—1.71[D]	—0.18[D]	. . . .	22	$Bi Cl_3$	Bi deposited.
0.0136	. . . .	. . . .	+2.01	28	$As Cl_3$	As deposited; no trace of $As H_3$ by $Ag NO_3$ test

D=Discharge potential, current passing.

[3] Sodium iodide was found to form with acetone a compound which exists in equilibrium with the acetone solution saturated with respect to itself below 14° C.; the compound crystallizes in long needles and has a composition corresponding to the formula NaI. $3(CH_3)_2CO$. It loses acetone in the air and reverts to NaI anhydrous. The transition value 14° C. was determined by measuring the vapor pressure of the system, NaI — $(CH_3)_2CO$ at various temperatures; on plotting a t—p curve, a nick was found at about 14° C. and it was observed that the long needles of NaI.$3(CH_3)_2CO$ had changed to the cubical anhydrous NaI just above 14° C. These measurements and the analytical data for the composition of the NaI.$3(CH_3)CO$ were lost in moving and have not yet been repeated.—(H. E. Patten.)

value for each metal during its deposition, which is near the value to be expected from theoretical considerations. The current density required to deposit each of these metals is 20 amperes N. D., or about 180 amperes per square foot. Iron required 20 amperes N. D., and copper 10 amperes N. D. for deposition, but when finally they came out at these high current densities the

TABLE II.

Decomposition Curves of Anhydrous Arsenic Trichloride[a] in Acetone.

Temperature 28° C.
Distance apart of electrodes = 3 cm.
Area of each Pt electrode = 3 sq. cm.

Curve I		Current Density Per Sq. Cm.	Curve II		Current Density Per Sq. Cm.
Volts	Amperes (*b*)	Amperes	Volts	Amperes (*c*)	Amperes
0.30	0.000012	0.000004	0.5	0.0003	0.0001
0.55	0.000087	0.000029	1.00	0.0008	0.00026
0.82	0.000197	0.000066	1.50	0.0017	0.00056
1.20	0.000395	0.000132	2.00	0.003	0.001
1.27	0.000546	0.000182	2.50	0.0042	0.0014
1.42	0.000622	0.000207	3.00	0.006	0.002
1.46	0.000740	0.000246	3.50	0.007	0.0023
1.51	0.000872	0.000290	4.00	0.0088	0.0029
1.63	0.00103	0.00031	4.50	0.0103	0.0034
1.74	0.00126	0.00042	5.00	0.012	0.004
1.79	0.00166	0.00055	5.50	0.0135	0.0045
2.01	0.00207	0.00069	6.00	0.015	0.005
2.07	0.00246	0.00082	6.50	0.016	0.00503
2.10	0.00289	0.00096	7.00	0.018	0.0060
2.61	0.00392	0.00131	7.50	0.0197	0.0069
3.36	0.00642*	0.00214	8.00	0.021*	0.007
			8.50	0.0225	0.0075
			9.00	0.0241	0.0080
			9.50	0.0257	0.0086
			10.0	0.027	0.009
			10.5	0.0285	0.0093
			11.0	0.030	0.010
			11.5	0.0314	0.0105
			12.0	0.033	0.011
			13.0	0.0356	0.0118
			14.0	0.0382*	0.0127*
			15.0	0.041†	0.0136†

(*a*) $AsCl_3$ dissolves with evolution of considerable heat. The concentration was about 10 per cent. by volume.
(*b*) Determined by potentiometer.
(*c*) Determined by milliammeter.
* No gas evolved.
† Battery point 2.01 volts for total cell at this current density.

coatings were smooth. Copper deposited from aqueous solution would be crystallized at current densities much lower than that used here—90 amperes per square foot.

Table II gives the current-e. m. f. curves obtained on electrolyzing a solution of arsenic trichloride in acetone. The total polarization shown by discharge was 2.01 volts, indicating that the arsenic deposit has a low single potential, as would be expected.

This work may be summarized:

1. Sodium and strontium metals have been deposited from saturated solution of the iodides in acetone at room temperature, using rather high current density.

2. Cadmium, tin, antimony, bismuth and arsenic have been deposited from solutions of their chlorides in acetone at moderately low current density.

3. Iron and copper were deposited from solutions of their chlorides (-ic.) in acetone at rather high current densities.

4. In most cases anode and cathode polarization values were obtained.

5. A new compound, NaI. $3(CH_3)_2CO$ is described.

This work was carried out in the University of Wisconsin, in the laboratories of Applied Electrochemistry and of Physical Chemistry jointly, and the authors wish to express their appreciation of the courtesy thus extended to them.

DISCUSSION.

Mr. Carl Hering: I would like to ask whether they have been able to deposit aluminum from such solutions.

Mr. W. R. Mott: Not from acetone solution. It is impossible to deposit aluminum from acetone solutions, or alcoholic solutions, so far as I have been able to determine. I have electrolyzed perhaps 25 solutions of aluminum chloride and other aluminum compounds, dissolved in these non-aqueous solutions. However, Dr. Patten has electrolyzed aluminum from its bromide solution in ethyl bromide.

Mr. E. F. Northrup: I would like to ask if the acetone solu-

tion was entirely free from all water molecules, and if it is true electrolysis in such a solution?

MR. MOTT: We have electrolyzed solutions of acetone and pyridine containing lithium chloride and varying amounts of water, and have observed practically two phenomena of interest. In the first place, with pyridine the least trace of water causes the cathode to become covered with an insulating film of organic nature, but unknown composition. In the second place, in the acetone solution, a very small addition of water will cause the separation of a second liquid phase which will contain a large excess of lithium chloride, this excess of lithium chloride removed from the acetone solution, leaving it so that it does not conduct nearly as well as before. We believe the acetone and pyridine used in our experiments were quite anhydrous—a thing we took considerable pains to verify.

MESSRS. L. S. PALMER AND R. C. PALMER (*Communicated*): During some work on the electro-deposition of antimony from antimony trichloride solutions in acetone, we noted that under certain conditions antimony was not deposited as pure metal but in the amorphous form known as explosive antimony. Some work is now in progress to determine the exact conditions which influence the formation of this deposit. The product in each case is being analyzed to determine the antimony trichloride content. It is hoped to report the results of this investigation at a subsequent meeting of the Society.

A paper presented at the Fifteenth General Meeting of the American Electrochemical Society, at Niagara Falls, Canada, May 7, 1909; President E. G. Acheson in the Chair.

ON THE ELECTROLYTIC REDUCTION OF NITRIC ACID.—II[1].

By Harrison E. Patten and W. J. McCaughey.

Introduction.

The authors present herewith experiments continuing the work previously reported to this society.[2]

In the first paper it was found that "nitrogen, either as free nitrogen or in the form of oxides, is given off at both copper cathode and platinum anode." Also, "it is probable that the reduction of nitric acid to ammonia at a copper cathode involves the formation of hydroxylamine as an intermediate stage." In the present research the action of the oxygen liberated at a platinum anode upon ammonium sulphate in sulphuric acid solution was studied to ascertain whether the ammonium salt is oxidized with the formation of gaseous products containing nitrogen, and single potential discharge measurements were made at the anode during the period of electrolysis. Copper sulphate was not added to the solution in this case, since it was desired to reproduce the end condition of the solution which is obtained when one reduces potassium nitrate in the presence of sulphuric acid and copper sulphate. The copper here is all deposited from solution before the reduction is complete.[3]

The second subject of study in this research is an attempt to obtain a more complete view of the course of the reduction of potassium nitrate in sulphuric acid solution in the presence of copper sulphate at a copper cathode, the method of attack being much the same as was followed in the first paper, as shown in Tables XXXII, XXXIII and XXXIV of Section VII. In the present research, however, more comprehensive analytical data

[1] Published by permission of the Secretary of Agriculture.

[2] Transactions American Electrochemical Society, **12**, 325 (1907).—"On the Electrolytic Reduction of Nitric Acid."

[3] In this present paper the tables containing the data will be numbered beginning with XL, so that a convenient reference may be made to the data in the first paper where the last table is numbered XXXIX. Similarly the figures in this present paper begin with No. 10, the last figure in the first paper being numbered 9.

were obtained for the solutions and the gases at anode and at cathode at a number of intervals during the electrolysis. Frequent observations upon the anode and cathode discharge potentials were made, both during electrolysis and in the intervals between the periods of electrolysis, while the anode and cathode products were being withdrawn for analysis.

Experimental Methods.

Electrical measurements. The current was measured on a Weston milliammeter. The discharge voltage at anode and at cathode was taken by momentarily interrupting the current during the process of electrolysis, and measuring by compensation the e.m.f. given by the electrode-solution-half-cell against two Lechanché dry cells whose voltage was obtained every few minutes by comparison with a Weston standard cell[4] whose value was 1.01900 at 25°. In this work the same half-cell was used as in the previous paper.[5] Its value (0.1 normal) as given by Palmaer is —0.5732 volt at 18° C.[6] The electrical connections used in all this electrolytic work are shown in Fig. 5 and described in detail on pages 335 and 336 of the first paper. The same galvanometer (portable d'Arsonval) was likewise used.

Electrolytic Procedure. The cell used for determining the anodic oxidation of ammonium sulphate in sulphuric acid solution was similar to that shown in Fig. 4 in the first paper.[7] The anode was of polished platinum, 5.72 square centimeters in area, fused into glass tubing, which served to give mercury connection. The anode was covered by a glass cylinder drawn out to a narrow opening at the top through which the anode gas could be drawn off and analyzed. The electrolytic cell used in the reduction of nitrate was slightly different from either of the cells previously used, and consisted of a circular glass crystallizing dish, 21 centimeters in diameter and 11 centimeters deep, which served to hold the solution, as shown in Fig. 10. In this dish were placed two flint glass reagent bottles, 8.5 centimeters in diameter, cut off at the bottom so that the remaining body of the

[4] This cell was numbered 118, Bureau of Standards collection, and was kindly loaned to us for this work. For temperature coefficient see Reprint No. 104 from Bulletin of the Bureau of Standards, Vol. 5, No. 2.

[5] *L. c.* "On the Electrolytic Reduction of Nitric Acid."

[6] Zeit. phys. chem., **52**, 129 (1907).

[7] *Loc. cit.*

bottle was about 12 centimeters in height. Each bottle was fitted with a two-hole rubber stopper, through which passed the glass tube giving mercury connection with the electrode inside the bottle, and a second tube which served to withdraw samples of gas and of electrolyte. These bottles served as anode and cathode chambers for the collection of the gaseous products of the electrolysis, and were held firmly in place by clamps attached

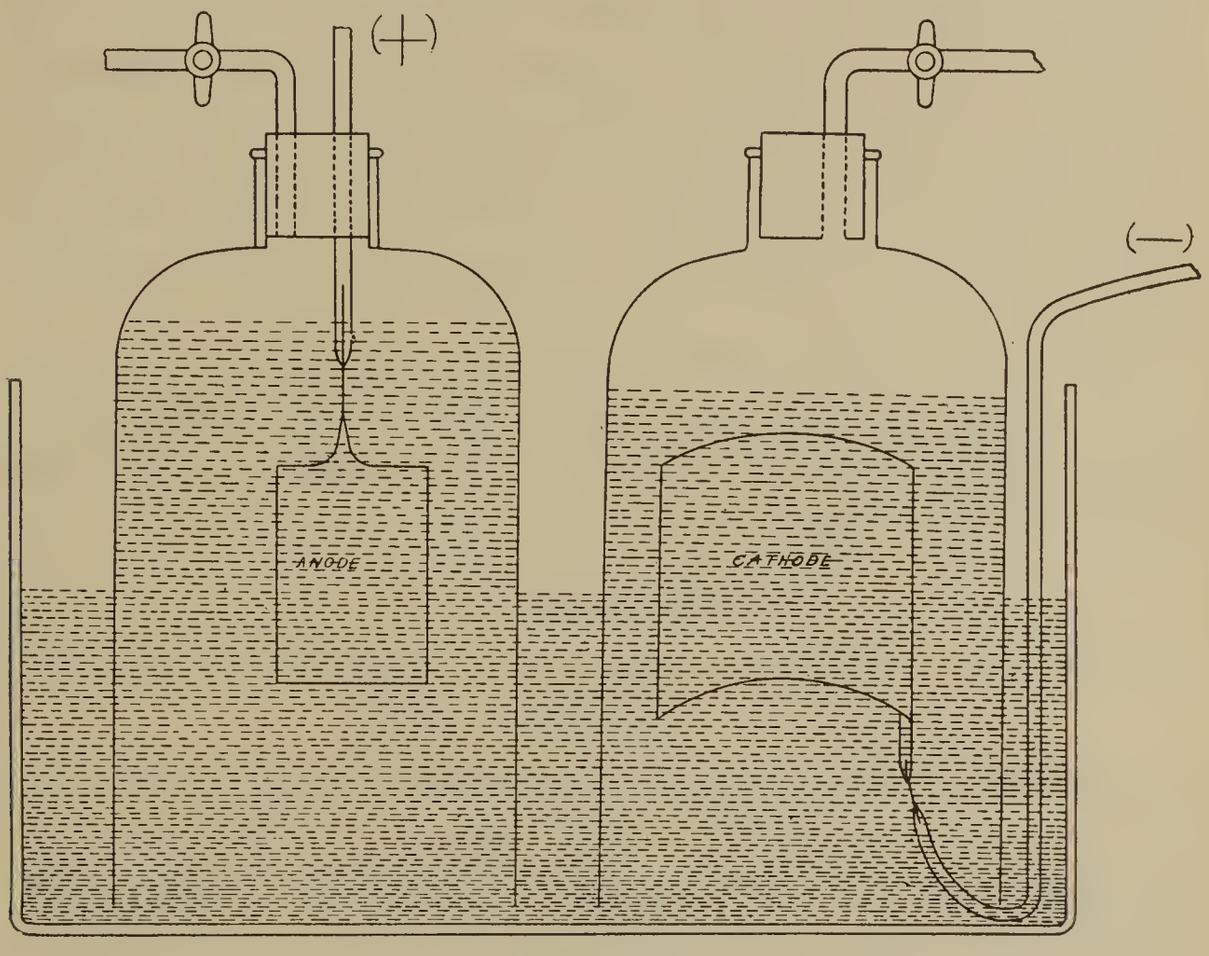


FIG. 10.

to a retort stand, thus preventing their rise and fall as the gas products collected within them.

Analytical methods. The ammonia formed in all of these reductions was determined by distilling the solution, previously made alkaline with caustic potash, into standardized acid, and titrating for the un-neutralized acid remaining. Since ammonia tends to form complex copper compounds with copper hydroxide, the copper present in the alkaline liquor was converted to sulphide by the addition of a few lumps of sodium sulphide. At the end of the ammonia determination this copper sulphide thus precipitated was filtered off, dissolved in acid, and in some cases deter-

mined electrolytically, and in others determined volumetrically by the cyanide method.

Determination of the gases. The anode gases were collected in a gas burette, measured accurately, absorbed by alkaline pyrogallol repeatedly, and the residual gas taken as nitrogen. There is good justification for this, since this residual gas when treated with phosphorus shows no further combustion, as would be the case if it contained oxides of nitrogen. In every case throughout this investigation the gas examined was analyzed within a few minutes after its generation, and for the anode gases the data are based on complete treatment of every bit of gas evolved; that is to say, samples were taken over each period of electrolysis, and the entire volume of gas itself was subjected to quantitative analysis.

The cathode gases were absorbed by palladium metal, the metal being repeatedly regenerated and the gas again passed over it until no further absorption of hydrogen took place. The residual gas is nitrogen.

Section XI.

Oxidation of ammonium sulphate in sulphuric acid solution at a platinum anode.[8]

A solution containing 0.4904 gram $(NH_4)_2SO_4$ in 150 c.c. of 1.715 per cent. sulphuric acid was made up. This quantity of ammonium sulphate (0.4904 gram) corresponds to 0.5000 gram KNO_3 when reduced quantitatively to ammonia, and contains 0.1040 gram of nitrogen. For convenience in the collection of anode gases this volume, 150 c.c., of solution was increased four-fold, to 600 c.c., each of the substances in solution being likewise increased to maintain the concentration as described.

This solution was electrolyzed in a beaker, using a copper cathode 100 sq. cm. total area, and a spiral platinum anode 5.72 sq. cm. in area. The anode gas was drawn off from time to time and analyzed for oxygen and nitrogen quantitatively. Anode and cathode discharge potentials were taken at intervals. The data thus obtained is given in Table XL, whose headings are self-explanatory.

When 22.9 c.c. of the gas left unabsorbed by alkaline

[8] For convenient reference, the sections in this paper begin with Section XI, the last section in the first paper on this subject being numbered X.

pyrogallol was treated with molten phosphorus it showed only a trace of oxygen. The volume after this treatment had changed to 22.8 c.c. at the same temperature and pressure as before, a loss of only 0.1 c.c., or about 0.44 per cent. by volume. The temperature was 23.5° C., and the pressure 772.2 mm. of mercury in all of the above measurements of gas volumes.

Corrected to 0° C. and 760 mm., allowing for aqueous vapor, the total nitrogen (38.1 c.c.) evolved at the anode reduces to 34.64 c.c., which weighs 0.04354 gram, taking 1 c.c. of nitrogen as weighing 0.001257 gram at 0°C. and 760 mm.

After 152.5 minutes electrolysis, 150 c.c. of the solution was found to contain 0.1025 gram nitrogen as ammonia, whereas the original content of nitrogen was 0.1040 gram for 150 c.c.—a loss of 0.0015 gram or 1.44 per cent. The nitrogen loss at the anode in gas form (0.04354 gram) when calculated for 600 c.c. of solution is about 10.5 per cent. of the total nitrogen. Two factors tend to make the loss of nitrogen from the solution appear less than is really the case: One, the loss of water by electrolysis, as hydrogen at the cathode and as oxygen at the anode; the other, surface evaporation of the electrolyte (approximately 57 sq. cm.)

Table XL.

Oxidation of ammonium sulphate in sulphuric acid solution at a platinum anode.

Total Time of Electrolysis		Period of Electrolysis		Gas Evolved	Gas not absorbed by Pyrogallol	Total Gas not absorbed by Pyrogallol	Total Oxygen	Current	Discharge Potential	
									Anode	Cathode (Copper)
Min.	Sec.	Min.	Sec.	c. c.	c. c.	c. c.	c. c.	Amp.	Volts	Volts
0	0	0	0	0	0	0	0	0	— 0.832	— 0.588
0	0	0	0	0	0	0	0	1.065	. .	. .
4	30	. .	. .	. .	. .	. .	. .	. .	— 2.044	. .
7	30	. .	. .	. .	. .	. .	. .	. .	. .	+ 0.180
16	30	16	30	53.2	3.0	3.0	50.2	. .	— 1.936	. .
41	30	25	0	95.2	6.0	9.0	139.4	. .	. .	. .
50	30	. .	.	. .	. .	. .	. .	. .	. .	+ 0.146
70	30	29	0	95.2	6.0*	15.0	228.6	. .	. .	. .
90	30	20	0	95.5	5.8	20.8	318.3	. .	.	. .
104	30	. .	. .	. .	. .	. .	. .	1.145	— 1.920	. .
110	30	20	0	95.7	5.2	26.0	408.8	. .	. .	+ 0.146
132	30	22	0	93.7	5.6	31.6	469.9	. .	. .	. .
151	30	. .	. .	. .	. .	. .	. .	. .	— 1.917	+ 0.250
152	30	20	0	94.3	6.5	38.1	584.7	1.145	. .	. .

* Determination lost by accident.

which is increased by evolution of gas and by a slight rise in temperature due to the heating effect of the electric current (to about 35° C.).

As seen in Table XL, 584.7 c.c. oxygen was liberated, weighing 0.770 gram,[9] and equivalent to 0.867 gram water, or about 0.9 c.c. for 600 c.c. of solution. Consequently this factor has a weight of only 0.15 per cent.

To estimate the effect of evaporation upon the diminution of volume, a solution identical with that used for electrolysis was made up, and 600 c.c. placed in the same beaker and allowed to evaporate, its surface being broken by air bubbles blown through the liquid under constant pressure at a rate near that at which gas was evolved during the electrolysis. The loss of water was found by weighing from time to time. At 30° C. this solution lost 0.9 c.c. per ten minutes, which is equivalent to 13.7 c.c. during 152.5 minutes, the total period of electrolysis in the run shown in Table XL. For rough approximation, 16 c.c. may be taken as the evaporation during electrolysis, a loss of 4 c.c. per 150 c.c. This would increase the nitrogen concentration of the solution so that if no loss occurred during electrolysis we ought to find 0.1068 gram of nitrogen per 150 c.c. The analysis then shows a deficiency of nitrogen in solution of approximately 0.0043 gram per 150 c.c., or 4.1 per cent.

The current during this run averaged 1.105 amperes, a current density at the anode of 0.193 ampere per sq. cm., or about 173.7 amperes per square foot. This is fairly representative of the current density used in the methods extant for the quantitative reduction of nitrates to ammonia at a copper cathode, using a platinum anode.

The discharge potential at the copper cathode suggests that hydroxylamine is formed at the anode by oxidation of ammonia, and diffuses to the cathode, where it acts as a depolarizer. The value given after 4.5 minutes of electrolysis is +0.180 volt at cathode; later this fell to +0.146 volt, which polarization persists for a considerable period. The withdrawal of gas samples for analysis disturbs the concentrations at both anode and cathode, consequently the rise of the cathode discharge to +0.250 volt near the end of the run does not mean that all of the hydroxylamine capable of being formed at the anode had been decomposed

[9] One c.c. oxygen weighs 0.0014384 gram at 0° C. and 760 mm.

at the cathode. It is very probable that a continuation of the electrolysis would show a drop in the cathode single potential to near its former value, +0.146 volt.

This probable formation of hydroxylamine at the anode is verified in the following section, where nitrate upon electrolysis gives hydroxylamine at *both* anode and cathode when the electrodes are kept in separate chambers.

Thus, it is evident that a solution of ammonium sulphate in 1.715 per cent. sulphuric acid when electrolyzed with platinum anode and copper cathode is decomposed, nitrogen *as such* being evolved at the anode. It is probable, too, that hydroxylamine is formed at the anode, diffuses to the cathode, is there decomposed, and thus gives a further loss of nitrogen in gas form.

Section XII.

A STUDY OF THE PROGRESS OF THE ELECTROLYTIC REDUCTION OF NITRATE IN ACID SOLUTION, USING COPPER CATHODE AND PLATINUM ANODE.

A solution containing 10 grams KNO_3 and 10 grams $CuSO_4.5H_2O$, was made up to 3,000 c.c., with sufficient sulphuric acid to give 1.715 per cent. H_2SO_4. This solution was electrolyzed in the cell described under the heading *Electrolytic Procedure,* and shown in Fig. 10. For the sake of convenience in publication, the electrical data, anode reaction masses and cathode reaction masses are given in three separate tables, XLI, XLII and XLIII; it must be remembered, however, that the data is all for the same solution, and in Figs. 11, 12, 13 and 14 this data is plotted on the same time axis (x) and all refers to the same reaction.

The anode was of polished platinum foil, 56.6 sq. cm. total area; the cathode, smooth sheet copper, 100 sq. cm. The temperature of the solution ranged between 22.5° and 25.0° C., the slight elevation above room temperature (22.5° C.) being caused by the heating effect of the current.

The anode and cathode single potentials were taken for some minutes before passing the current, and then electrolysis was allowed to proceed for short periods, at first for ten minutes, and samples of anode and cathode solution and the total gases were taken; the discharge potentials were then read and the

current sent through the cell again. Later the periods of electrolysis were increased to twenty minutes each, and finally to runs of over an hour each, as shown in the tables.

TABLE XLI.

Electrical data. Reduction of nitrate in sulphuric acid solution. Platinum anode, 56.6 sq. cm. area; copper cathode, 100 sq. cm. area.

Remarks	Time	Current	Period of electrolysis		T'al time of electrolysis		Interval		Discharge Single Potential		Temperature of solution	Coulombs
									Anode	Cathode		
	A.M.	amperes	min.	sec.	min.	sec.	min.	sec.	volts	volts	°C.	
No gas coming	11:41	0.000	0	0	0	0	0	0	—0.844	—0.440	22.9	
from anode or	P.M.											
cathode	12:08	0.000	0	0	0	0	27	0		—0.440	22.9	
	12:12	0.000	0	0	0	0	31	0	—0.952		22.9	
Current on	12:16:30	1.030	0	0	0	0					22.9	
Gas from cath-	12:16:40		0	10	0	10						
ode in minute	12:18	1.050	1	30								
bubbles scatter-	12:20:30		4	0	4	0				—0.324	22.9	
ed over surface	12:21		4	30	4	30			—2.219			
of cathode												
Current off	12:26:30		10	0	10	0						628.2
	12:27								—1.666	—0.528	22.9	
Interval	1:20						57	0	—1.521	—0.440		
Current on	1:23:30	1.030			10	0				—0.368	22.5	
	1:32:30				19	0			—2.078			
Current off	1:33:30		10	0	10	0					22.7	618.0
	1:58									—0.412		
Interval	2:01						31	30	—1.577			
Current on	2:05	1.030			20				—2 073		22.5	
	2:10:30				25	30				—0.325		
	2:15	1.015			30	0					22.8	
	2:18	1.050			33	0					22.8	
	2:20	1.015			35	0				—0.296		
	2:22:30	1.050			37	30						
	2:23				38	0			—2.116			
	2:24	1.045			39	0						
Current off	2:25		20	0	40	0					23.0	1362.8
	2:26								—1.782	—0.397		
	2:47								—1.634			
Interval	2:49									—0.389	22.9	
Current on	2:50	1.045			40	0	25	0	—2.103	—0.290	22.9	
	2:57	1.015			47	0						
	2:58	1.045			48	0					23.3	
	2:59:30	1.015			49	30						
	3:08:30				58	30				—0.290		
Current off	3:10	1.045	20	0	60	0			—2 103		23.6	1242.6
	3:13									—0.339		
	3:39									—0.210		
Interval	3:41						30	0	—1.491		23.1	

Remarks	Time P. M.	Current amperes	Period of electrolysis min. sec.	T'al time of electrolysis min. sec.	Interval min. sec.	Discharge Single Potential Anode volts	Discharge Single Potential Cathode volts	Temperature of solution °C.	Coulombs
Current on	3:42	1.015		60 0					
	3:48	1.013		66 0					
	3:50			68 0				24.2	
	3:51	1.045		69 0					
	4:24			102 0		—2.116			
	4:27			105 0			—0.267		
	4:47			125 0			—0.267		
	4:49			127 0		—2.116			
Current off	4:50	1.0105	68	128 0				25.0	4228.4
	4:56					—1.722			
	4:57						—0 414		
	5:45						—0.388		
Interval	5:46				59 0	—1.490		23.7	
Current on	5:49	1.065		128 0				23.7	
	5:58			137 0			—0.296		
	5:59	1.090		138 0					
	6:05	1.090		144 0					
	6:07			146 0		—2.216			
	6:11			150 0			—0.266		
	6:32	1.070		171 0					
	6:37			176 0		—2.278			
	6:39			178 0			—0.108		
	6:41	1.065		180 0					
	6:51	1.070		190 0					
	6:57			196 0		—2.216			
	6:58			197 0			—0.050		
Current off	7:00		71	199 0				24.6	4591.6
	7:25				25 0	—1.562			
Interval	7:27				31 30		—0.456	24.1	
Current on	7:31:30	1.065		199 0				24.1	
	7:36			204 30		—2.201			
	7:37	1.070		205 30					
	7:39			207 30			—0.164		
	8:28	1.065		255 30		—2.216	—0 121		
Current off	8:37:30		66	265 0					
	9:07						—0.427		4536.7
Interval	9:08				33	—1.349		23.8	
Current on	9:10	1.080		265 0					
	9:13			268			—0.129		
	9:16:30			271 30		—2.143			
	9:21	1.080		276					
	9:30			285			—0.121		
	9:33			288		—2.157			
	9:49			304			—0.093		
	9:55	1.080		317				24.7	
	10:02			324		—2.186			
	10:03	1.085		325				24.5	
	10:28			343			—0.064		
	10:30			345		—2.156			
	10:32	1.065		347					
Current off	10:33		83	348					5384.0
	10:57					—1.387		24.9	
	10:59				26 0		—0,400		

The anode and cathode gases were analyzed at once as described in the discussion on analytical methods. The samples of solution were immediately titrated with permanganate to estimate the hydroxylamine and to destroy it in such a manner as to prevent its decomposition adding to the ammonia content of the solution. The concentration of the $(NH_2OH)_2SO_4$ was too low to permit the use of Fehling's solution. The ammonia formed was determined by distillation from alkaline solution (NaOH) and titration of the un-neutralized standard acid in

TABLE XLII.

Anode reaction masses. Reduction of nitrate in sulphuric acid solution. Platinum anode, 56.6 square cm. area; copper cathode, 100 square cm. area.

Total Period of Electrolysis	Oxygen as Gas		Nitrogen as Gas		Nitrogen in Solution		Copper in Solution
	Increment	Total	Increment	Total	As NH_2OH	As NH_3	
Min.	gr.	gr.	gr.	gr.	Grams per 50 c.c. sol.	Grams per 50 c.c. sol.	Grams per 50 c.c.
0	. . .	. . .	. . .	. . .	0.000000	0.00000	0.04276
10	0.0323	0 0323	0.00396	0.00396	0.000000	0.00014	0.0419
20	0.0377	0.0700	0.00395	0.00791	0.000000 Trace	0.00028	0.0460
40	0.0764	0.1464	0.00609	0.01400	0.000019[a]	0.00056	0.0424
60	0.0806	0.2270	0.00660	0.0206	0.000019	0.00042	0.0378
128	0.3190	0.5460	0.0187	0.0393	0.000038[b]	0.00042	(lost)
199	0.3440	0.8900	0.0148	0.0541	0.000038	0.00056	0.0413
265	0.3310	1.2210	0.0144	0.0685	0.000038	(lost)	0.0393
348	0.4286	1.6496	0.01572	0.08422	0.000057	0.00135	0.0373

a One drop K Mn O_4 solution used.
b Two drops K Mn O_4 solution used.

which the ammonia distillate was caught. Most of the ammonia determinations were made the same day, but a few final titrations were left over till the next day, owing to the difficulty of following the change in color of cochineal indicator at night. The copper content was determined from the residues left after the distillation of ammonia; the copper sulphide was dissolved in nitric acid, this acid driven off by evaporation with sulphuric acid, and the copper separated from manganese (introduced in the hydroxylamine estimation) by deposition upon aluminium metal, re-dissolved and determined by the cyanide method.

Table XLI contains the anode and cathode discharge single

potentials, current, temperature of solution and time readings, as shown by the various column headings.

Tables XLII and XLIII give the anode and cathode reaction products, the gases evolved being reduced to 0° C. and 760 mm., allowing for aqueous vapor and calculated to grams. The NH_2OH and NH_3 are expressed as grams of nitrogen, to facilitate comparison with the gaseous nitrogen. The copper is given as grams of copper left in solution.

Table XLIII.

Cathode reaction masses. Reduction of nitrate in sulphuric acid solution. Platinum anode 56.6 square cm. area; copper cathode, 100 square cm. area.

Total Period of Electrolysis Min.	Hydrogen as Gas		Nitrogen as Gas		Nitrogen in Solution		Copper in Solution
	Increment gr.	Total gr.	Increment gr.	Total gr.	As NH_2OH Grams per 50 c.c. sol.	As NH_3 Grams per 50 c.c. sol.	Grams per 50 c.c.
0	. . .	. . .	. . .	. . .	. .	. . .	0.04276
10	0.0000611	0.0000611	.00610	0.00610	0.00010	0.00070	0.0382
20	. . .	. . .	. . .	. . .	0 00020	0.00247	0.0409
40	. . .	. . .	. . .	. . .	0.00026	0.00332	0.0320
60	. . .	. . .	. . .	. . .	0.00029	0.00416	0.0343
128	0.0001089	0.000170	0.00041	0.00651	0.00020	0.00740	0.0309
199	0.000387	0.000557	0.00138	0.00789	0 00029	0 0108	0.0255
265	0.001493	0.00205	0.00259	0.01048	0.00026	0.0133	0.0215
348	0.00580	0.00785	0.00675	0.01723	0.00029	0.01536	0.0193

From Tables XLII and XLIII additional data was derived by calculation. In Table XLIV is given the total nitrogen content of the solution in the electrolytic cell after each period of electrolysis, account being taken of the nitrogen abstracted in solution (as sample for analysis) and in gas form at both anode and cathode. Having obtained this average total nitrogen content of the solution *at the end* of each period of electrolysis as shown in column V, Table XLIV, the total nitrogen in solution at the beginning of each period was obtained by adding the proportionate loss (for 50 c.c. of solution) of gaseous nitrogen at anode to get the anode concentration, column VII, and by adding the proportionate loss of nitrogen in gas form at the cathode for the cathode concentration, column XIII. These values for

anode and cathode concentrations are, of course, only approximations. Still they serve to give a basis for calculating the per cent. of total nitrogen which has been transformed. The values of anode and cathode concentration cannot be obtained because of the complex diffusion processes at work in the cell, which

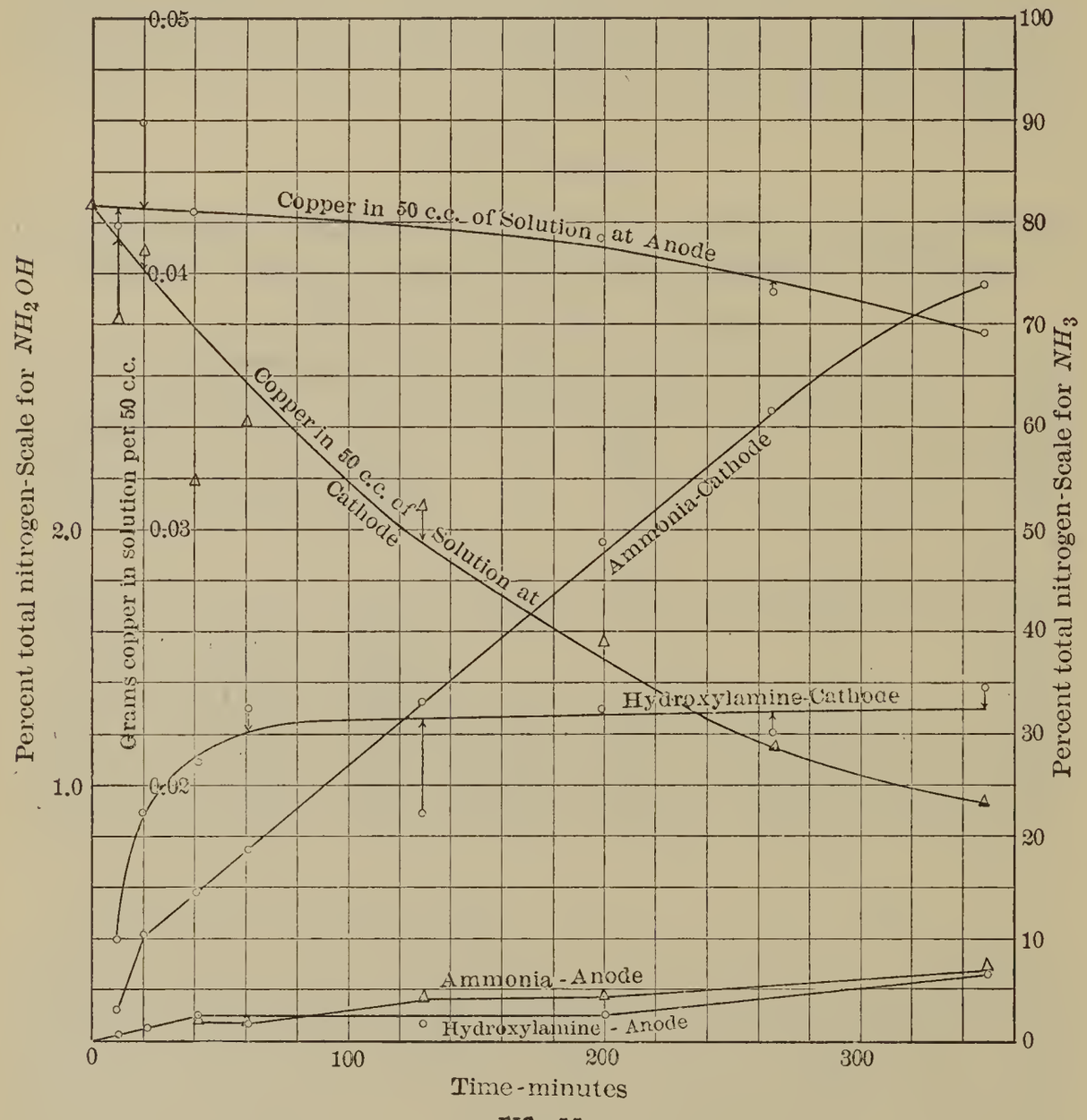


FIG. 11.

are enhanced by the stirring produced in each electrode compartment by the gas evolved during electrolysis as well as by the withdrawal of samples for analysis.

However, when the per cent. of nitrogen present as hydroxylamine and as ammonia is represented graphically, using time in minutes as abscissa and per cent. total nitrogen as ordinate, very regular curves are obtained both for anode products and for cathode products. These curves are shown in Fig. 11, the

scale for hydroxylamine (per cent.) being given at the extreme left, while the per cent. scale for ammonia is placed at the right and is condensed in order to show the full curve. On this same plate the grams of copper in solution in 50 c.c. of anode liquor and of cathode liquor are also given, the scale being placed at the left of the figure inside the first scale (for hydroxylamine). Fig. 12 contains curves for the total grams of anode and cathode

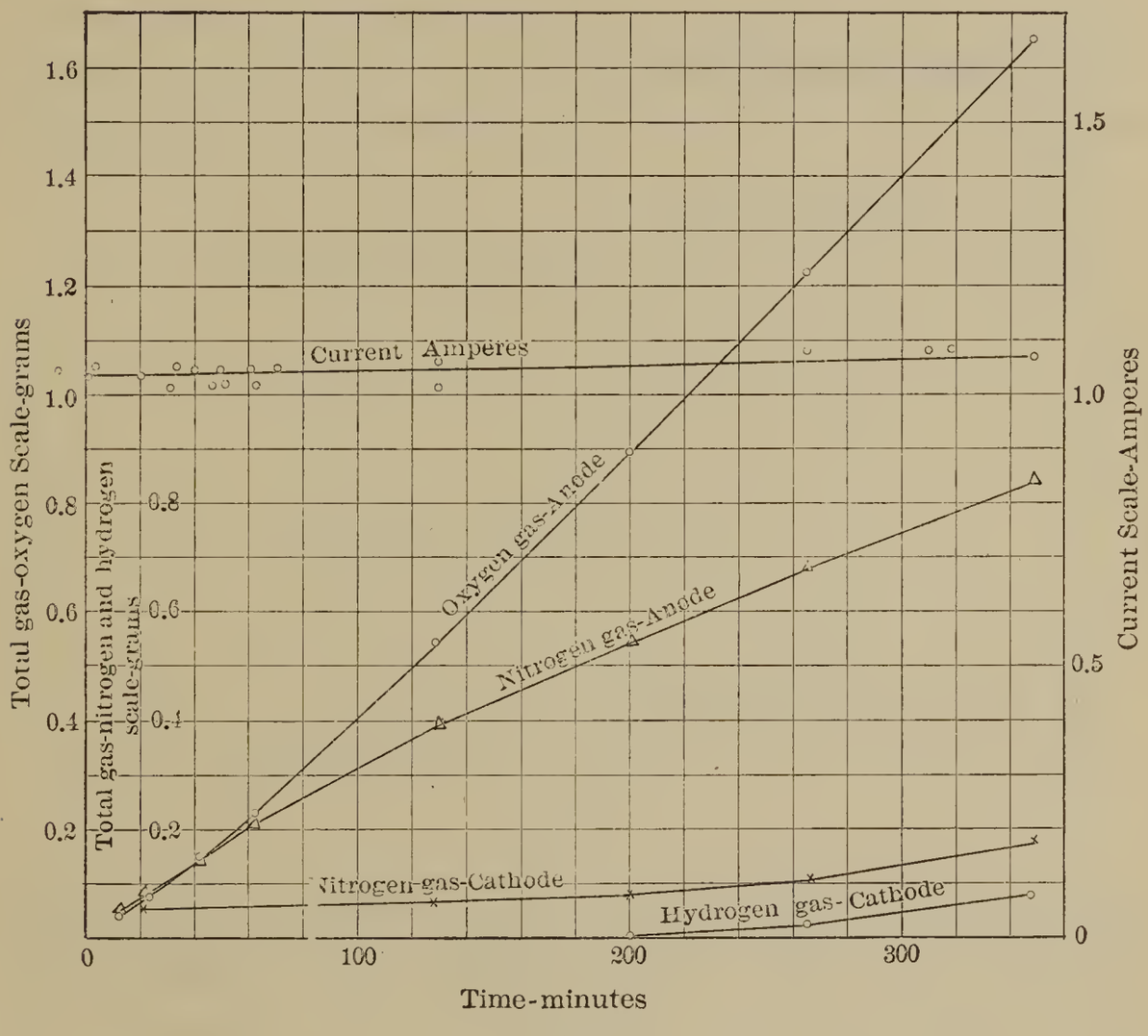


FIG. 12.

gases liberated during electrolysis, as shown by their respective lettering. The scales for oxygen and for nitrogen and hydrogen are different—see legends at the left of the figure. The current in amperes is shown on the same plate; its scale is at the right. For strict comparison the coulombs should appear, but the apportionment of the coulombs between the several products of electrolysis will be discussed later and treated on a separate sheet of curves.

The discharge potentials at anode and at cathode are shown

in Fig. 13, two curves being given for each electrode; one given by momentarily interrupting the current and taking the discharge voltage; the other by reading the single potential of the electrode against the solution after electrolysis had ceased for some time during the taking of samples for analysis. Fig. 13 contains in addition, cathode and anode discharge potentials obtained in section XI during the electrolysis of ammonium sulphate in sul-

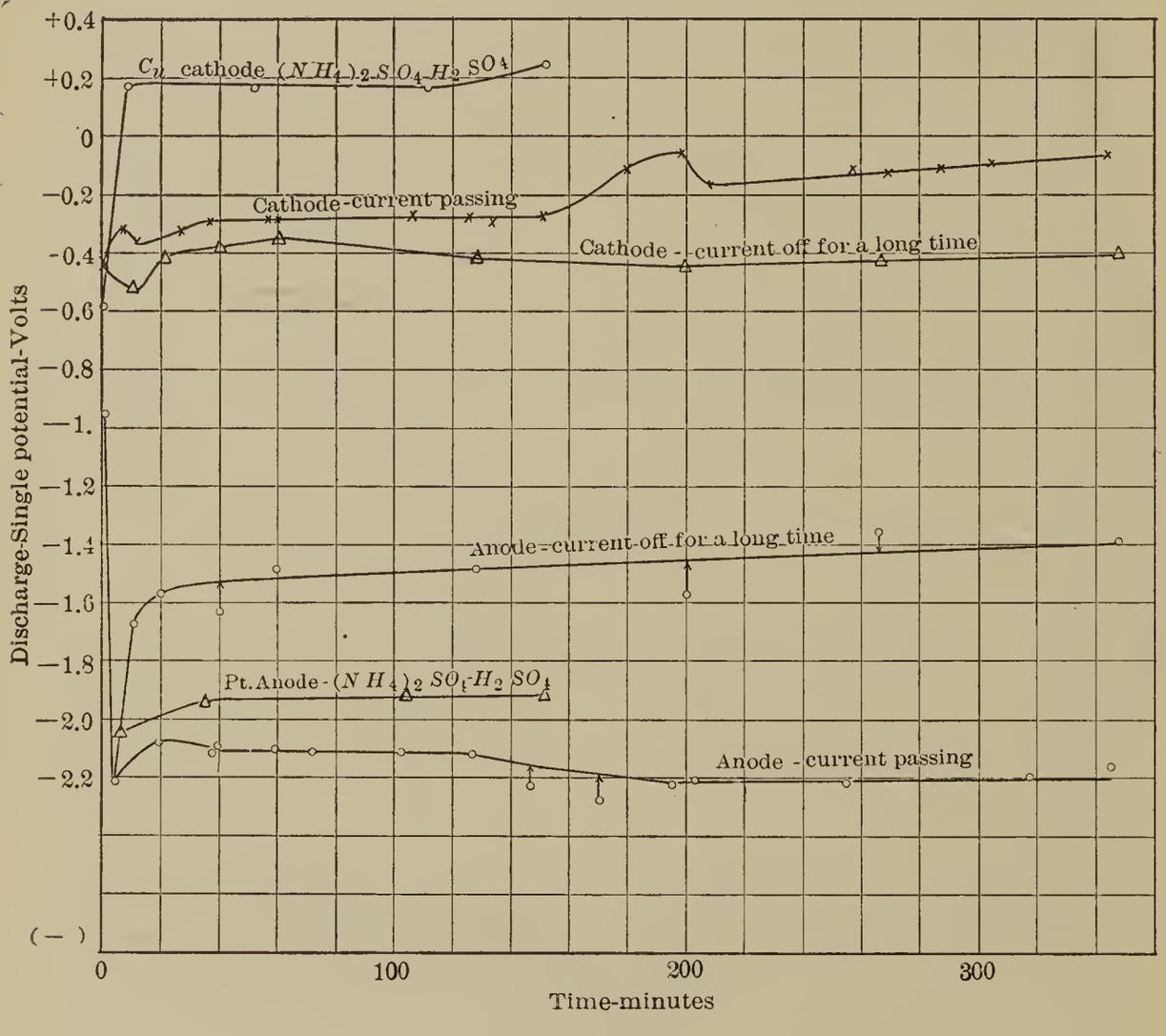


FIG. 13.

phuric acid solution, using copper cathode and platinum anode, see Table XL. These last two curves show the end values which the anode and cathode discharge potentials may be expected to reach after all the nitrate is reduced.

Discussion of results. Anode reactions: From the data in Tables XLII and XLIV, and the graphs in Figs. 11 and 12, it is seen that after ten minutes of electrolysis under the stated conditions, 0.6 per cent. of the total nitrogen in the anode liquor appears as ammonia, and after ten minutes more of electrolysis

this ammonia concentration has risen to 1.2 per cent. Meanwhile the nitrogen lost as nitrogen gas at the anode is 0.3 per cent. of the total during the first ten minutes, and the same during the second ten minutes. From the analytical data above it would appear that no hydroxylamine was formed at the anode during the first twenty minutes, and only a trace of it is detected after forty minutes. But it is likely that some hydroxylamine was formed by oxidation of the ammonia, and then further oxidized to nitrogen and possibly to oxides of nitrogen, since at a platinum anode hydroxylamine is actually broken down to nitrogen. This probability of the formation of hydroxylamine as an intermediate

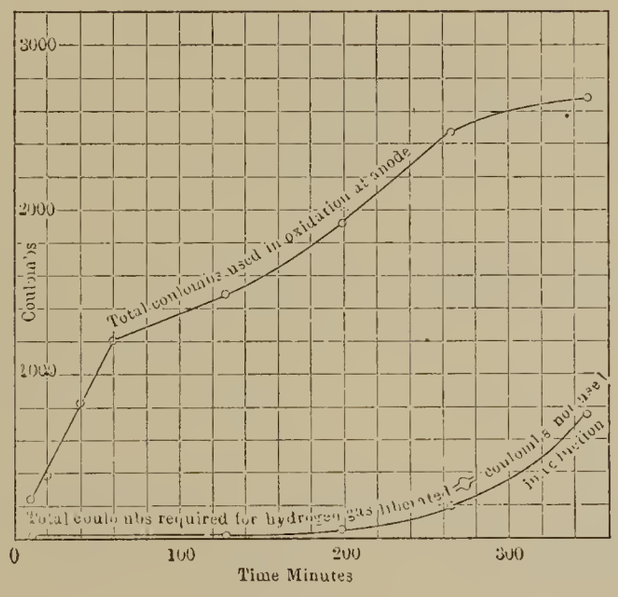


FIG. 14.

stage in the oxidation of ammonia at a platinum anode is confirmed by the single potential discharge from the anode during the first twenty minutes of electrolysis, as shown in Fig. 13, the polarization values being below —2.0 volts, which is very close to the polarization at a platinum anode given by hydroxylamine in sulphuric acid solution with sulphate in solution—see Table XXVII and Fig. 7, curve 3, in the first paper. Later hydroxylamine was found in the anode liquor in slightly increasing concentration as electrolysis proceeded, until at the end of the run 0.275 per cent. of the total nitrogen was present as hydroxylamine, while 6.49 per cent. of nitrogen remained as ammonia. During the last period of electrolysis (eighty-three minutes) 1.5 per cent. of the total nitrogen was lost at the anode in gas form.

TABLE XLIV.

Derived data on anode and cathode reaction products in the reduction of nitrate.

I	II	III	IV	V	VI	(Anode) VII	VIII	IX	X
Total Period of Electrolysis. Minutes	Total Solution Left. c.c.	Nitrogen Lost as Gas, Anode and Cathode Increment. Grams	Total Nitrogen Left in Entire Solution. Grams	Total Nitrogen in 50 c. c. Solution. (Average of Anode and Cathode Liquor) Grams.	Loss of Nitrogen Gas at Anode. Increment per 50 c. c. Solution. Grams	[v + vi] Total Nitrogen in 50 c. c. of Solution at Start of Each Period of Electrolysis. Grams	Nitrogen in Solution at Anode as NH_2OH in 50 c. c. Grams	[viii ÷ vii] Per cent. of Total Nitrogen as NH_2OH in Anode Liquor	Nitrogen in Solution at Anode as NH_3 in 50 c. c. Grams
10	3000	0.001006	1.38561	0.023077	.000066	0.023143	. . .	. . . . .	.00014
20	2900	0.01304	1.33845	0.02297	.000068	0.023038	. . . . .	. . . . .	.00028
40	2800	0.026160	1.28635	0.02286	.000108	0.022968	.000019	0.083	.00056
60	2700	0.006675	1.23447	0.022737	.000122	0.022859	.000019	0.083	.00042
128	2600	0.01893	1.18226	0.022373	.000360	0.022733	.000038	0.167	.00042
199	2500	0.01618	1.11865	0.02205	.000296	0.022346	.000038	0.17	.00056
265	2400	0.01701	1.05837	0.021690	.000300	0.021990	.000038	0 172	Lost
348	2300	0.02247	0.99086	0.02080	.000342	0.022882	.000057	0.275	.00135

I	XI [x ÷ vii]	XII	(Cathode) XIII [v + xii]	XIV	XV [xiv ÷ xiii]	XVI	XVII [xvi ÷ xiii]	XVIII [vi ÷ vii]	XIX [xii ÷ xiii]
Total Period of Electrolysis. Minutes	Per cent. of Total Nitrogen as NH_3 in Anode Liquor	Loss of Nitrogen Gas at Cathode Increment per 50 c. c. of Solution. Grams	Total Nitrogen in 50 c. c. of Solution at Start of Each Period of Electrolysis. Grams	Nitrogen in Solution at Cathode as NH_2OH in 50 c. c. Grams	Per cent. of Total Nitrogen as NH_2OH in Cathode Liquor	Nitrogen in Solution at Cathode as NH_3 in 50 c. c. Grams	Per cent. of Total Nitrogen as NH_3 in Cathode Liquor	Per cent. of Total Nitrogen Lost at Anode as Gas	Per cent. of Total Nitrogen Lost at Cathode as Nitrogen Gas
10	0.606	0 000103	0.02318	.00010	0 42	.00070	3.03	0.283	0.445
20	1.215	. . . .	0 02297	.00020	0.87	.00247	10.75	0.295	
40	2.44	. . . .	0.02286	.00026	1.14	.00332	14 51	0.47	
60	1.84	. . . .	0.022737	.00029	1.28	.00416	18.25	0.533	
128	1.85	0 000007	0.02238	.00020	0.90	.00740	33.1	1.57	
199	2 51	0.0 00027	0.022053	.00029	1.32	.0108	49 0	1.32	
265	Lost	0 c00054	0.021744	.00026	1.20	.0133	61.6	1.383	
348	6.49	0 0000145	0.020815	.00029	1.29	.01536	73 8	1.39	

TABLE XLV.

Apportionment of coulombs during reduction of nitrate.

I	II	III	IV	V	VI	VII	VIII	IX	X	XI	XII	XIII	XIV
Period of electrolysis	Total period of electrolysis	Coulombs increment (milli-ammeter)	Coulombs equivalent to oxygen liberated	Coulombs used in oxidation at anode	Total Coulombs passed	Total Coulombs equivalent to oxygen	Total Coulombs used in oxidation at anode	Coul'bs equivalent to nitrogen at anode $[N = 1\frac{1}{2}O]$ NH_3	Coul'bs equivalent to nitrogen as NH_2OH at anode $[N = \frac{1}{2}O]$ NH_2OH	Coulombs equivalent to hydrogen gas	Coulombs equivalent to hydrogen gas	Coulombs used in reduction	Coulombs used in reduction
Min.	Min.		Each peroid	Each period				Each period	Each period	Each period	Total	Each period	Total
10	10	628.2	393	235.2	628.2	393	235.2	143.1	47.8	5.8	5.8	622.4	622.4
10	20	618.0	455	163.	1,246.2	848	398.2	143.0	47.7	(0.88)		617.1	1,239.5
20	40	1,362.8	923	439.8	2,609.0	1,771	838.0	220.8	73.6	(1.77)		1,361.	2,600.5
20	60	1,242.6	974	268.6	3,851.6	2,745	1,106.6	239.1	79.7	(1.77)		1,240.8	3,841.3
68	128	4,228.4	3,851	377.4	8,180.0	6,596	1,484.0	678.	226.	(6.1)	16.2	4,222.3	8,063.6
71	199	4,591.6	4,153	438.6	12,771.6	10.749	1,922.6	537.	179.	38.7	54.9	4,552.9	12,616.5
66	265	4,536.7	3,996	540.7	17,308.3	14,745	2,463.3	522.	174.	143.1	198.0	4,393.6	17,010.1
83	348	5,384.0	5,174	210.0	22,692.3	19,919	2,673.3	570.	190.	556.0	754.0	4,828.0	21,838.1

Examination of the polarization at a platinum anode in potassium nitrate, copper sulphate and sulphuric acid solution shown in Fig. 8, Table XXXIX (first paper), curve 2, indicates that the anode polarization in Fig. 13 is due to oxidation of hydroxylamine and of ammonia rather than to oxidation of nitrite, the nitrite anode polarization being higher during the first stages of electrolysis than that of ammonia or of hydroxylamine when copper sulphate is present in solution. The anode single potential, when no current is passing (Fig. 13), is slightly below that of oxygen—1.400 volt. The ammonia in the anode chamber, of course, diffuses over from the cathode.

Fig. 12 contains curves for the total grams of oxygen and of nitrogen evolved at the anode. The curve for oxygen is not a straight line, since part of the oxygen is used in oxidation processes, which cause the liberation of the nitrogen. In Table XLV is given an approximate estimate of the apportionment of the coulombs which passed through the cell during electrolysis. Column V shows the coulombs apparently used in oxidation at the anode during each period of electrolysis. The curve for the total quantity of nitrogen gas evolved at anode is very regular (Fig. 12), and one might expect that the curve for the total coulombs used in oxidation would show a corresponding regularity, but this is true only of the first portion of the curve (see Fig. 14) during the first sixty minutes of electrolysis. The reason for this break in the curve of coulombs at sixty minutes evidently (see Fig. 11 and Table LXIV, columns IX and XI) is that the oxygen acts on both hydroxylamine and on ammonia.

In Table XLV, columns IX and X give the coulombs equivalent to the nitrogen evolved during each period of electrolysis, assuming: First, that this nitrogen comes entirely from the oxidation of ammonia (column IX), where 14.01 grams nitrogen are liberated by 24 grams of oxygen [$N \fallingdotseq 3/2O$]; and, second, that this nitrogen is produced by oxidation of hydroxylamine, only eight grams of oxygen being required for 14.01 grams nitrogen [$NH_2OH + 1/2O = N + H_2O + 1/2\ H_2O$]. During the first period of ten minutes the coulombs used in oxidation (235.2) is sufficient to account for the nitrogen gas liberated, whether one considers it as coming from the oxidation of ammonia or

from hydroxylamine. Besides this (143.1 coulombs for oxidation of ammonia) there remain 92.1 coulombs unaccounted for. It must be remembered that the solution used in this experiment was practically free from gases in solution at the beginning of electrolysis, and some of the anode oxygen undoubtedly remained dissolved in the anode liquor. This is probably one reason why the oxygen apparently used in oxidation is less in the second ten minutes' run than in the first ten, while the nitrogen gas evolved is the same quantity at both periods. Toward the end of the run one sees that the coulombs used in oxidation are barely sufficient to account for the nitrogen as an oxidation product of ammonia; and later, even much lower than required by the equation $NH_3 + 3/2O = N + H_2O + 1/2H_2O$. Evidently the two processes are going on side by side, and as we have no data on the relative preponderance of one over the other, it is impossible to assign the fraction of the coulombs which is proper to each. It is interesting to note that during the last period of electrolysis (eighty-three minutes) the coulombs (190) equivalent to the nitrogen liberated, considering it as derived from the oxidation of hydroxylamine, was 90.5 per cent. of the coulombs apparently (210) used in oxidation.

In all, approximately 8.7 per cent. of the total nitrogen was liberated at the anode during 348 minutes of electrolysis.

The copper remaining in solution at the anode is given in Table XLII, last column, and shown graphically in Fig. 11.

Cathode reactions: Hydroxylamine formed as an intermediate step in reduction of nitrate. The striking fact brought out by this part of the research is that hydroxylamine is formed as an intermediate stage in the reduction of nitrate to ammonia. Comparison of the data in Tables XLII (anode), XLIII (cathode) and XLIV (derived data) shows that after ten minutes of electrolysis 0.42 per cent. of the total nitrogen was present as hydroxylamine, this value being based upon the permanganate titration, and that it could not have diffused over from the anode within that period is certain, since not a trace of material oxidizable by permanganate was found in the anode liquor until the current had been passing forty minutes, and then only a trace.

During the first ten minute period of electrolysis 3.03 per cent. of the total nitrogen is converted to ammonia, while 0.44 per

cent. of the nitrogen is liberated in gas form at the cathode. For the next 118 minutes the reduction is most efficient, only 0.30 per cent. of the nitrogen being lost as cathode gas, and only 0.0001089 gram hydrogen being evolved, whereas 0.0000611 gram hydrogen gas was given off in the first ten minutes. The curve for cathode discharge potential in Fig. 13 confirms this analytical data, in that the effect of hydrogen polarization is not noticed until some 160 minutes of electrolysis have passed; and even then, when the sample of solution was removed from the cathode chamber for analysis, thus renewing the solution about the electrode, the hydrogen polarization is no longer in evidence. The discharge potentials for copper cathode in ammonium sulphate in sulphuric acid, in Fig. 13, just above the cathode discharge curve for this nitrate reduction, show what polarization may be expected when all nitrate has been reduced to ammonia.

The cathode curves for NH_3 and NH_2OH in Fig. 11 show a decrease in the rate of formation of ammonia and of hydroxylamine with time; but the ammonia is formed at a constant rate, the concentration steadily increasing after the first twenty minutes, while the hydroxylamine approaches a concentration which after sixty minutes remains practically constant during the rest of the run. Bearing in mind that the concentration of the cathode chamber is changed every time a solution sample is removed for analysis, it seems evident that the hydroxylamine tends to form in sufficient quantity to maintain a certain concentration at the cathode in equilibrium with the other reaction masses. And, too, from the fact that practically no nitrogen or hydrogen is liberated during 118 minutes of electrolysis after the cathode equilibrium is nearly established, it may be inferred that while the concentration of hydroxylamine remains at a certain value it is reduced almost quantitatively to ammonia, and very little nitrogen produced in its decomposition. It may be, also, that with the nitrate radical present in sufficiently high concentration, the hydroxylamine is converted to ammonia as fast as formed, leaving the already formed hydroxylamine intact. This would explain why under certain conditions Tafel[10] was unable

[10] Zeit. anorg. Chem., **31**, 289 (1902); also **56**, 375 (1907).

to reduce hydroxylamine at a copper cathode, and why Flaschner[11] with low current density found a very small fraction of the hydroxylamine reduced, whereas with favorable conditions it is possible to reduce up to 65 per cent. of the hydroxylamine to ammonia at a copper cathode in sulphuric acid solution containing copper sulphate. Evidently the nitrate is converted in considerable quantity to hydroxylamine at the beginning of electrolysis. This hydroxylamine then is reduced and nitrogen liberated. But when the concentration of hydroxylamine falls to that required by equilibrium conditions we have a smooth reduction of nitrate, very little hydroxylamine being left over.

Loss of nitrogen at cathode. During the first ten minutes of electrolysis 628 coulombs passed; of this quantity 5.8 coulombs were used in the liberation of hydrogen, the remainder (99 per cent.) being used in reduction. In this same period 0.0061 gram of nitrogen gas was evolved, but the coulombs required in this case cannot be calculated, since the mechanism of the reduction of hydroxylamine with the formation of nitrogen gas is unknown. It is possible that the nitrogen may be formed by direct oxidation of hydroxylamine, thus:

$$4NH_2OH + O_2 = 2N_2 + 6H_2O,$$

the oxygen coming from the nitrate.

In Fig. 11 the gradual decrease in concentration of copper in solution at the cathode is shown, as grams copper per 50 c.c. of solution. For the reasons just stated, this gives only a rough idea of the quantity of copper deposited, and it will be noted that owing to necessarily incomplete stirring of anode and cathode chambers during the taking of samples, some of the concentrations of copper actually obtained are considerably below the average concentration indicated for the cathode liquor by the general curve shown in Fig. 11.

It is interesting to note that the cathode polarization shown in Fig. 13 for this reduction of nitrate indicates a predominance of hydroxylamine reduction, during the first ten minutes, by a rise toward the polarization value given by hydrogen; this value drops back again as the reduction settles into the later

[11] Monats. Chem., 28, 209 (1907); also V. Rothmund u. Flaschner, Zeit. anorg. Chem., 58, 183 (1908). See also, Owen L. Shinn, Jour. Am. Chem. Soc., 30, 1378 (1908).

stage, in which during 118 minutes there is practically no gas evolution from the cathode.

Fig. 14 shows the coulombs used in liberating hydrogen gas during the electrolysis, together with the coulombs used in oxidization at the anode.

Summary.

In this paper it is shown:

(1) That ammonium sulphate in sulphuric acid solution is oxidized at a platinum anode, nitrogen gas being liberated.

(2) That in the electrolysis of nitrate in sulphuric acid solution containing copper sulphate, hydroxylamine is formed at the copper cathode as an intermediate step in the reduction of nitrate to ammonia; that nitrogen gas is liberated at the cathode; that the ammonia which diffuses over from the cathode is oxidized at the anode to substances which reduce permanganate; that nitrogen gas is evolved at the platinum anode.

(3) The electrical and chemical and physical conditions under which these changes take place are defined.

(4) It appears that nitrogen undergoing either oxidation or reduction probably goes through several of the intermediate stages, if not all, which exist between its initial and final state of oxidation.

Addendum.

To determine whether nitric oxide (NO) is given off at the copper cathode during reduction of nitrate under the conditions given in Section XII, a separate experiment was carried out with a fresh portion of the *same* solution used for the electrolysis in Section XII. This solution—about 3,400 c.c., containing $CuSO_4$, KNO_3 and H_2SO_4, in the proportions stated in Section XII—was electrolyzed in the same apparatus shown in Fig. 10, and with the same copper cathode and platinum anode. The cathode gas was withdrawn, after a current of 1.15 amperes had passed for one hundred and five minutes, measured over mercury in a burette, and treated with oxygen. There was no brown coloration of the gas observed, consequently no appreciable quantity of nitric oxide was present. A 50 c.c. portion of solution from

the cathode chamber required 0.4 c.c. of 1 N. permanganate to oxidize it. After a second one-hundred-and-five-minute period of electrolysis, 35.4 c.c. cathode gas at 23.5° C. was treated over mercury with 35.8 c.c. of oxygen gas (95.6 per cent. oxygen; 4.4 per cent. nitrogen) and the resulting gas volume found to be 71.4 c.c. at the same temperature. The barometer read 768.8 mm. and may have varied slightly during the experiment. No brown color was visible in the gas and no contraction in volume took place, consequently the quantity of nitric oxide formed in this electrolytic reduction of nitrate is negligible. The total quantity of gas from each of these experiments was shaken with 2 per cent. NaOH solution, evaporated to dryness and tested for nitrates colorimetrically, using the phenoldisulphonic acid method,[1] but even this delicate test gave no indication of nitrate. A portion of the NaOH solution of cathode gases when oxidized with H_2O_2 in alkaline solution also gave no test for nitrate. It would seem, therefore, that the nitrogen lost at the cathode is in the form of nitrogen gas.

In this second run of one hundred and five minutes the current was constant at 1.15 amperes, and the cathode liquor showed only a slight increase in hydroxylamine concentration, 50 c.c. requiring 0.46 c.c. of 1 N. permanganate.

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U. S. Department of Agriculture,
Washington, D. C.

[1] See Bull. No. 31, p. 39. Bureau of Soils, U. S. Dept. Agriculture (1906).

A paper prescnted at a meeting of the New York Section of the American Electrochemical Society, March 1, 1909, and presented in abstract by C. I. Zimmerman, at the Fifteenth General Meeting of the Society, at Niagara Falls, Canada, May 8, 1909. President E. G. Acheson in the Chair.

ELECTROCHEMICAL METHODS IN SOIL INVESTIGATIONS.[1]

By F. K. Cameron.

In studying the soil in relation to its crop producing power, it is clear that the point of contact between soil studies and plant studies is the soil solution, *i. e.*, the soil moisture, which is a solution of the organic and inorganic materials in the soil and the soil atmosphere. Strictly speaking, we need give no further consideration to the plant than to bear in mind that the plant root is always moving so long as the plant lives. The characteristic feature of our modern soil investigations is that we regard the soil from the dynamic rather than from the static point of view, and realize that the soil atmosphere and the solid portions of the soil are in constant motion, and more especially that the soil solution is constantly moving.

When water flows upon the soil, some of it runs over the surface and disappears in the neighboring drainage channels. This portion of the water is now designated as the "run-off." Some of the water goes back into the atmosphere by evaporation, and this is known as the "fly-off," while a third portion passes into the soil, and is known as the "cut-off." The cut-off becomes the soil solution. It passes down through the soil, mainly through the force of gravity, and in so passing it proceeds through the larger soil openings and remains but a comparatively short time in contact with any particular soil grain, and thus in this passage takes up a small but variable amount of the mineral and organic material which the soils yield to solution. Some of this cut-off passes on through the sub-soil and

[1] An address given by invitation of the New York Section, March 1, 1909. Published by permission of the Secretary of Agriculture.

again appears at the surface in the form of springs, seepage water, etc., and mingles with our rivulets, brooks, creeks and rivers, so that all our waters of this character are in effect soil solutions, but of widely varying concentrations. With the cessation of the rainfall and the beginning of evaporation at the surface, there commences a return movement of a portion of the cut-off water toward the surface upon which it fell. This continual drying out of the soil particles at the surface causes a capillary pull or drag upon the water within the soil, and this water rises through the very finest pore spaces of the soil and over the soil grains in films, the water being longer in contact with the soil, dissolving material from them and taking up the dissolved material from the capillary spaces, and this material is brought to the surface in a more or less effective way, depending mainly upon the physical composition of the soil. It will be observed that we can thus subdivide the cut-off water into gravitational water and capillary water, the gravitational water dissolving but little of the soil material, for it passes only through the larger spaces, and diffusion from the smaller spaces in passing is exceedingly limited and generally negligible, while on the other hand the capillary water rising toward the surface itself dissolves and takes up much more soluble material throughout the capillary spaces and soil films.[2] It is this water with which the plant has to deal, and it will be seen that it is constantly bringing material for plant nutrition from the depths in the soil—sometimes much below that to which plant roots ever penetrate. Thus it becomes obvious that the chemistry and physics of the soil as related to crop production is primarily a solution study,[3] and, speaking generally, the electrochemical methods which have proved effective in studying solutions elsewhere are all more or less applicable to soil studies.

A few moments' consideration will show, moreover, that the physics and chemistry of the soil solution are no less important in developing a consistent and rational knowledge of the engineering properties of soils than for agricultural purposes, and a study of the soil solution is one of the great fundamental problems of applied physics and chemistry. Time will not permit developing

[2] Bull. Nos. 9, 10, 23, 30, Bureau of Soils, U. S. Dept. Agr. Means: Science, **15**, 33 (1902).

[3] Bull. Nos. 17, 18, 30, 52, Bureau of Soils, U. S. Dept. Agr.

this subject in any detail here, but it has seemed worth while to call attention to some of the methods and apparatus which have thus far been found useful in the laboratories of the Bureau of Soils.

One of the most useful instruments which has been devised for soil work[4] is a slide wire bridge, of a form which can be readily carried into the field for observations there as well as in the laboratory. The essential feature of this bridge is a circular wire so calibrated that the ratio of the bridge arms is read directly, and by a special attachment a slight turn of the wrist will enable one to read resistances of 10 to 100 ohms, from 100 to 1,000 ohms, and from 1,000 to 10,000 ohms. The whole apparatus, with dry battery induction coil, telephone and other attachments, is conveniently packed in a small case measuring 8 x 7 x 7 inches and weighing approximately six pounds. In areas where there is an accumulation of soluble salts or "alkali," the amount of alkali in the soil can be determined approximately by mixing so much distilled water with the soil as it will take up without allowing any free water to flow from it—in other words, saturating the soil—placing the saturated soil in a hard rubber cell of known dimensions, fitted with parallel electrodes. These electrodes each form a part of the cell and are then slipped between spring contact-clips on the bridge box and the resistance read off, the temperature of the wet soil being taken at the same time by means of a small thermometer. The saturation of the soil is accomplished with great readiness and precision after a little practice, as well as the estimation of the texture of the soil; with this data the salt content of the soil can be readily read off from tables previously prepared. Of course, more accurate work can be done if a special table or curve be prepared for the particular mixture of salts encountered in the field, and it is our practice, when field parties are surveying an area containing alkali, to prepare such a curve for them in the laboratory after the analysis of typical samples of the salt bearing soils from the area in question. The exact *modus operandi* is described in the publication of the Bureau of Soils entitled, "Soil Survey Field Book, Field Season, 1906," pages 24 to 41.

As the salt content of a soil, when it is present in considerable

[4] Bull. Nos. 8, 15, Bureau of Soils, U. S. Dept. Agr.

amounts, can be determined with fair accuracy by this bridge method, many attempts have been made to use it for the converse problem of determining the moisture content of the soil,[5] in other words, to use the bridge as a soil hygrometer. But serious difficulties have made this method of doubtful application to the problem. In the first place, when the concentration of the soil solution is dilute, as it is in the soils of ordinary humid areas, a small translocation of dissolved electrolytes becomes relatively important, and such frequent standardization of the apparatus becomes necessary that the method has but little advantage over a direct gravimetric laboratory determination. But more important perhaps is the fact that no method has yet been devised by which a good contact between buried electrodes and the soil can be maintained. As pointed out at the beginning of this paper, the solid soil particles are themselves continually in motion. The soil is always either shrinking or expanding, and in doing so is constantly changing its volume, the change in volume being accompanied by a marked hysteresis.[6] There is no doubt that an effective hygrometer for soil work would be one of the most valuable instruments that could be invented for many engineering as well as agricultural investigations. This bridge promises more success as a practical instrument, for field work at least, than any other so far suggested, but it must be admitted that in its present shape the method is very faulty.

The variation in the dielectric constant of the soil with the moisture content has also been used to estimate the water in soils.[7] Experiments have been made by Dr. Briggs and Dr. Buckingham in this bureau, using Drude's method, with the soil in the end condenser and a wave length of from 50 to 200 cm. The results showed that the specific inductive capacity of the soil varies sufficiently with the water content and is independent of the concentration of the soil solution up to such concentrations as occur under natural conditions in the soil. Further experiments were made similar to Hertz's original experiments with a wire rectangle[8] and to the experiments of Rubens and

[5] Bull. No. 15, Division of Soils, U. S. Dept. of Agr., page 10 (1899).
[6] Bull. No. 50, Bureau of Soils, Dept. of Agr.
[7] "Methods of Soil Hygrometry," The Physical Review, **22**, 248 (1906).
[8] Wied. Ann., **31**, 421 (1887).

Arons.[9] Waves from an oscillator enter a divided circuit, and after traversing the two arms, meet at the spark micrometer, where the sparking is a minimum if the same time is required for the waves to traverse each arm. If one arm of the circuit is led through the ground, the point at which the waves must be introduced in order to give a minimum sparking at the spark micrometer varies with the wetness of the soil; and by gravimetric calibration the readings of the instrument may be interpreted in terms of the percentage of water in the soil surrounding the soil arm of the circuit. These experiments were of a preliminary character and have not as yet developed a practical method of determining the soil moisture.

The bridge has also been calibrated as a thermometer,[10] using various resistances whose temperature coefficients have been accurately determined, and for this purpose has proven of enormous value, not only in determining soil temperatures in the field and in laboratory experiments, but the temperature of the soil and the air above the soil in greenhouse work, temperatures of rivers and lakes at various depths, the heating of stored hay, tobacco, etc. It can be readily seen that it is a great convenience for the investigator to read his temperatures without leaving the desk in his office during the course of an experiment that may be going on in the laboratory, greenhouse or field some considerable distance away.

Another very interesting and important application of the bridge has been in the observation of dissolved material abstracted from solution, as, for instance, in the absorption and retention of soluble fertilizer ingredients from the soil solution by the solid particles of the soil. Without attempting to describe these investigations in detail, I will say that it has been shown that the fertilizer material may be absorbed upon the soil grain surfaces in the condition of a very concentrated layer of solution, and in this condition it will still conduct the current,[11] whereas the dry fertilizer salts themselves will not conduct the current. This lends peculiar confirmation to the hypothesis that the fertilizer material when absorbed from the solution by the soil is not

[9] Wied. Ann., **42**, 581; **44**, 206 (1891).

[10] Bull. No. 15, page 27, Division of Soils, U. S. Dept. of Agr. (1899).

[11] Bull. No. 52, p. 42, Bureau of Soils, U. S. Dept. of Agr. (1908); Electrochem. and Met. Industry, **5**, 257 (1907).

rendered available to growing plants, but rather exists as a concentrated solution subject to drafts upon it by the plant roots growing in the more dilute free solution of the soil.

In connection with the absorption studies there arise most interesting problems connected with the suspension of the finer solid particles of the soil, and these in turn are more or less directly connected with the very practical problems of flocculation, deflocculation, soil erosion, translocation, physical condition, etc. It is claimed by some investigators that all these problems are more or less complicated by the presence in the soil of colloidal materials, meaning thereby coagulated gel or jelly-like material which coats the soil grains, and it has been suggested that the migration of gels under the influence of the current could be used as a method of research in these problems. It has, however, been shown by direct experiment in our laboratories that substances which cannot by any possibility form a gel, such as rutile, hematite, etc., when ground very fine and suspended in water, migrate under potential difference, and this led to very interesting speculations as to the possibility of a correlation of the dielectric properties[12] of the solid components of the soil, with their susceptibility to remaining in suspension, sedimentation, etc., which has already been reported to this Society.

Conversely it has become evident that when the solid particles, gels or otherwise, be kept fixed, the solution itself will move under the current, and in a proper device will exhibit the well known phenomenon of electrical endosmosis.

A very interesting application of this to soil studies has been made, for evidence has been adduced from which a conclusion has been drawn that in the process of solution—owing to hydrolysis of the silicate and similar minerals of the soil—colloidal decomposition products coat the soil grains and prevent further solution.[13] Theoretically this position seems unsound, for by definition the colloid is of such nature that diffusion could take place through it, though perhaps more slowly than in the pure liquid. However, the hypothesis was tested directly by placing the ground rock or soil mineral between the walls of

[12] Trans. Am. Electrochem. Soc., **9**, 265 (1906).

[13] Bull. 92, Bureau of Chemistry (1905); see also the one-diaphragm cell of Verdet, Am. Chim. Phys. [3] **37**, 242 (1853).

two cylindrical cells[14] made of unglazed porcelain. The inner cell was fitted with a metal tube (in our experiments it was generally block tin), the tube being perforated with a small opening to permit the escape of gas.

Using this cell we were able to show that the process of solution of soil minerals is continuous. The electrical endosmosis carries the solution toward the cathode compartment, and after a time the solution drips from the block tin cathode tube into a beaker containing phenolphthalein, which is immediately turned red, showing the presence of alkali derived from the dissolved mineral. The solution found in the outer anode chamber of the cell now contains acid radicals, such, for instance, as phosphoric acid, when a soil is dissolved. The importance of this evidence to soil chemistry lies mainly in the assurance thus furnished that soil particles are continually passing into solution, and that the soil is not *solely* dependent upon indefinite complex and slow processes of weathering and decomposition, due to carbonic acid and organic acids, for the supply of soluble materials which support the growth of plants from year to year. As a matter of fact, the great weathering agent is water itself.

A further application of electrochemical methods of measurement is found in the quantitative estimation of various metals by electroanalysis, using the various standard methods of depositing metals, as well as the anode oxidation and cathode reduction processes where they may apply. Occasionally the measurement of electrode single potentials is found desirable. In this case the standard method of measurement, using the Ostwald calomel electrode as a half cell, together with Pogendorff's compensation method for reading the electromotive forces, is used. Diagrams and detailed description of this method are given in the paper already presented to this society at the New York meeting in 1907.[15]

Another application of the Ostwald half-cell to soil problems may be made for the determination of the concentrations of dissolved material held close to the soil grain surfaces. Two half-cells also may be opposed to each other through a solution of known concentration, this solution being divided into two

[14] Bull. No. 30, p. 27, Bureau of Soils, Dept. of Agr. (U. S.), (1905).
[15] Transactions, 9, 325.

portions by a plug of finely divided soil material or finely ground solid whose absorption effect is to be studied. Thus the potential difference between the very concentrated layer of solution at the soil grain surfaces, and a solution whose concentration is known, may be accurately determined, both with respect to magnitude and sign. So far as we are aware, this method has found application rather in purely theoretical electrochemistry, but it offers a means of confirming results obtained by electrical conductivity measurements which show the existence of absorbed material in concentrated solution close to the surface of the soil grains.

The time allotted me by the program forbids further descriptions, but, in conclusion, it may be emphasized that all of the physical and electrical measurements which can shed light upon solution processes are required to answer the numerous and complex questions which arise in our study of soil and soil waters.

Bureau of Soils, U. S. Department of Agriculture,
Washington, D. C.

DISCUSSION.

MR. HERING: I would be interested to know how Dr. Cameron gets over the difficulties of the losses at the electrodes. It seems to me that in measuring the resistance of a material like that the losses at the electrodes become extremely important, especially if, as has been done by many writers, it is represented in ohms. When one represents volts in terms of ohms one generally gets into trouble. I mention that because I had a similar problem some time ago,[1] and found this method worked very well, if used in accordance with the well known principle of the potentiometer, that is, if the drop of voltage is measured at two potential points; knowing the cross-section, the current which flows through, the drop of potential between the two points, and their distances apart, one can calculate the resistance even of a liquid. In that case you must use gold for the potential points, and not

[1] See "Liquid Potentiometer," Hering, Trans. Am. *Inst. El. Eng.* **19**, 317 (1902).

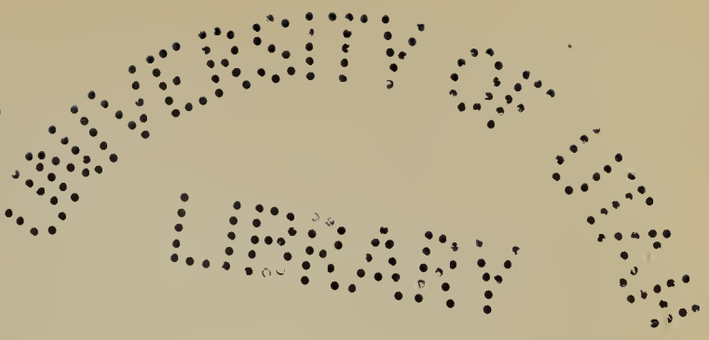
platinum, because the latter occludes gases, and this vitiates the results.

Dr. F. K. Cameron (*Communicated*): I have no doubt that Mr. Hering is quite right in pointing out that there are important losses at the electrodes, and if the actual resistances of the soils were, in themselves, of any importance they would have to be taken into account. In that case I should certainly avail myself of his experience. But I think he has misunderstood my problem, namely, to put into the hands of our field men a method and an instrument by which, knowing the texture of a soil, and the average percentage of water in a saturated soil of that texture, they can by resistance measurements quickly approximate the quantity of soluble salt present. The whole process is predicated on empirical measurements, contains several more or less obvious sources of error, is confessedly of doubtful utility for soils containing very small quantities of soluble salts, but does, as a matter of experience, give results of sufficient approximate accuracy in mapping soils in the field.

Of course, for rigidly accurate measurement of the electric resistance of solutions, it is necessary to use an interrupter of extremely high frequency, such for instance as a Leyden jar. All the measurements made by the much used Kohlrausch method are open to the same objection; and where very dilute solutions are measured, involving high resistance, it is undoubtedly true that the figure obtained is a composite one, part of its value being due to the resistance of the liquid and part to the electrolytic capacity at the electrodes.

In some recent experiments in our research work it has been found advisable to use a wheel, having a number of make and break contacts on its periphery. By driving this wheel at a high speed, much higher interruptions were obtained than those given by the ordinary induction coil, used in experiments by the Kohlrausch method.

A paper read at the Fifteenth General Meeting of the American Electrochemical Society, at Niagara Falls, Canada, May 8, 1909; President E. G. Acheson in the Chair.



OVER-VOLTAGE AS A FACTOR IN THE CORROSION OF METALS.

By William Roy Mott.

The commonly accepted theory of the corrosion of metals is that it is principally due to local galvanic couples formed by the metal and its impurities. On this basis the amount of this local current corresponds with the amount of corrosion. The local current depends on three factors, namely, the resistance of the local circuits, the electrochemical voltage of the same as a primary cell, and the voltage required to liberate hydrogen on the cathode. The resistance of the circuits consists of two parts: first, there is the resistance of the electrolyte between the electrodes, which depends on their distance apart and their respective areas, as well as the concentration and temperature of the electrolyte; second, a resistance results from the formation of poorly conducting films. As regards the electrochemical voltage of the circuits this will be greater the more electropositive the anode, and the more oxidizing agents available at the cathode. The voltage required to liberate hydrogen is our last factor, and this depends on the nature of the impurity that forms the cathodes of the local circuits as well as the nature of the electrolyte. From an acid solution hydrogen separates at a much lower potential than from an alkaline solution. Some metals, such as platinum and gold, with the same electrolyte allow hydrogen to be electrolyzed out at a much lower voltage than certain other metals, such as mercury, cadmium and zinc. This phenomenon has been called over-voltage, and its bearing on the corrosion of metals is illustrated by the following facts.

In 1833, A. Bouchardat[1] made some experiments on the corrosion of zinc in vessels of different metals which showed that

[1] See Tommasi, Traite d' Électrochimie, p. 198.

the particular metal in contact with the zinc was important in determining the amount of the corrosion. Some of this data is given in the accompanying Table No. I:

TABLE I.

Corrosion of Zinc Balls by Dilute Sulphuric Acid in Vessels of Different Substances:

Nature of Vessel	Amount of Corrosion	Calculated Over-voltage
Glass	3	Insulator
Sulphur	3	Insulator
Tin	12	+0.55
Lead	28	+0.50
Antimony	38	+0.45
Bismuth	38	+0.45
Gold	102	+0.20
Silver	115	+0.15
Platinum	116	+0.15
Iron	130	+0.10
Copper	150	Reference Standard
Brass	190	—0.14

In the above table there is given the corrosion according to Bouchardat. This series of figures has, apparently, never been discussed for the purpose of showing the reason for their order. A preliminary survey shows that metals like tin and lead with high over-voltage decreased the rate of corrosion compared with metals of low over-voltage like copper and platinum. So a quantitative consideration of the influence of over-voltage on the corrosion was then tried. In each electrical circuit the same acid and arrangement were used, and therefore the amount of corrosion, being proportional to the current, times a constant and the resistance, is equal to the cell voltage minus the over-voltage.

Let V equal the cell voltage of a zinc-copper couple in sulphuric acid. Its voltage is about six-tenths (0.6) volt.

R equals the resistance of circuit and includes the factor of proportionality between corrosion currents and corrosion.

C equals corrosion current.

O equals over-voltage referred to copper as cathode.

Our formula becomes as follows:

$$CR = V - O.$$

Corrosion times a constant is equal to the cell voltage minus the over-voltage. With the above data and the formula, calculation can be made as to possible excess voltage for the cathode metals. Such data is given in the table.

The corrosion of zinc as influenced by its impurities is a great industrial problem that enters into the use of galvanized ware and in many other places. Zinc containing iron, copper or platinum is evidently going to corrode very rapidly. Zinc that has been placed in platinic chloride solution corrodes more rapidly than in any other metal salt, because the platinum that separates allows hydrogen to be evolved at the lowest voltage.

Is there any metal that we could place with the zinc in order to counteract the influence of such impurities as iron? The ordinary suggestion, in answer, would be to amalgamate the zinc, which effectually protects it. But as mercury costs $0.50 a pound, this is somewhat expensive. The principle appears to be to add a metal on which hydrogen separates with difficulty. Such metals are cadmium, lead, tin and mercury.

Caspari has designated as over-voltage the excess voltage required to cause the first hydrogen bubble to appear, as compared with a platinized platinum electrode. His values were as follows:

TABLE II.

Over-voltage of Hydrogen on Metals.

Pt. (platinized)	0.005	Pd.	0.48
An	0.02	Sn.	0.53
Pt. (polished)	0.09	Pb.	0.64
Ag.	0.15	Zn.	0.70
Cu.	0.23	Hg.	0.78

This work is hardly a criterion of what would happen at high current densities, say 100 amperes per square foot, which is a general order of magnitude of current density used in practical electrolysis. With this end in view, the author has made some preliminary experiments in which only the cathode metal was varied. Such work bears on the proper cathode material to use in water electrolysis and is important in the electrolysis of sodium chloride where hydrogen is one of the products.

Ostwald and Roskowski have proposed a theory that the smooth-

ness of the cathode is all important in determining its over-voltage. It was therefore planned to secure several metals with as nearly identical surface conditions as possible. This was done by casting the metals, zinc, cadmium, lead, tin, antimony and bismuth in hot glass specimen tubes and allowing them to cool slowly from the bottom. In this way, as good an imitation of a liquid surface as possible was secured. With the exception of the antimony, all castings were very smooth.

The data for the current voltage curve in half normal sulphuric acid is given in the following Table No. III. The anode was in each case the same platinum plate (area about 5 square inches), surrounding the centrally placed cathode.

TABLE III.

Amperes	Tin Volts	Tin Plated with Copper Volts	Lead Volts	Zinc Volts	Cadmium Volts	Bismuth Volts	Antimony Volts	Magnesium Volts
0.10	2.92	2.50	3.02	2.92	3.10	3.20	2.73	3.73
0.20	3.04	2.63	3.20	3.06	3.28	3.37	2.90	3.83
0.30	3.15	2.72	3.26	3.18	3.40	3.53	3.07	3.93
0.40	3.25	2.80	3.33	3.29	3.52	3.68	3.17	4.00
0.50	3.32	2.89	3.40	3.38	3.60	3.80	3.30	4.05
0.60	3.38	2.96	3.50	3.46	3.69	3.93	3.40	4.15
0.70	3.46	3.03	3.58	3.53	3.78	4.07	3.50	4.22
0.80	3.52	3.10	3.65	3.60	3.86	4.16	3.60	4.29
0.90	3.59	3.16	3.69	3.67	3.95	4.26	3.70	4.36
Area	2 sq. in.	2 sq. in.	2 sq. in.	1½ sq. in.	1 sq. in.	¾ sq. in.	¾ sq. in.	2 sq. in.

Low melting metals, zinc, lead, cadmium, tin, bismuth, require about the same excess voltage and evidently would be very unsatisfactory for use in electrolytic cells where hydrogen was to be given off with a minimum of energy. On the other hand, they would be very good to use where extra work was to be done at the cathode, as in organic reductions and in the production of arsine. Also, they would be valuable for preventing corrosion of metals.

Referring again to Table No. I, we note a remarkable position for brass. Some experiments on its over-voltage would seem desirable. A brass rod was tested and gave results as low as iron, nickel, cobalt and platinum; I would suggest that a brass cathode would be more economical of power than an iron one.

The reason for brass acting this way is not clear. A suggestion would be that it would tend to corrode with the production of a fine grained surface similar to platinized platinum, and hence the low over-voltage. In some unpublished data that was once obtained by Dr. Patten and the author, an amalgamated copper cathode showed a remarkable change in over-voltage with continued electrolysis. At first it showed the high over-voltage of mercury and its amalgams, but after several hours of electrolysis its over-voltage was considerably less than that of the original copper plate. Perhaps the repeated formation and decomposition of copper hydride was the cause of the changes. In several papers on electro-organic reductions, the cathode metal has been observed to change in behavior with continued use.

The nature of over-voltage has not been made clear. We observe that most metals of very high melting points, such as platinum, iron, nickel and cobalt have low over-voltage. All metals having low melting point, we have seen from data given here, have high over-voltage. This relationship is in the direction that the smoothness of a metal is greater the less it is removed from its melting point. That the smoothness of the surface is the only factor, does not seem correct. All metals that have low over-voltages absorb hydrogen in large amounts, while all metals that do not absorb hydrogen have high over-voltages. Hence, the metal seems to act as a carrier of hydrogen from the place of entry of the current to a convenient point where a bubble may form without undue amount of energy in starting the same. Hence, we propose two bases for predicting the possible over-voltage of a metal: First, the empirical rule of low melting point and high over-voltage; second, the low power to absorb hydrogen and high over-voltage.

In this paper we have shown that the electrolytic view of corrosion of metals becomes more useful as the factor called over-voltage is included. Quantitative relations are shown for some simple cases of corrosion. Predictions of what alloying metal would afford most protection appears somewhat possible. Tin and zinc are the two metals most used in protecting iron and steel articles. These metals have high-over-voltage, which is a guiding principle in designing non-corrosion metal combinations. The metals, lead, tin, cadmium, zinc and mercury, are to be

recommended for preventing corrosion because they tend to prevent the liberation of hydrogen on their surfaces.

The connection of the author with the Department of Analytical Chemistry of the University of Wisconsin, has aided in securing materials for this work, which was done with apparatus kindly loaned by the Department of Electrochemistry.

A paper presented at the Fifteenth General Meeting of the American Electrochemical Society, at Niagara Falls, Canada, May 8, 1909; President E. G. Acheson in the Chair.

THE PROBABLE ELECTRICAL NATURE OF CHEMICAL ENERGY.

By A. H. Patterson.

In a recent paper Dr. J. E. Mills has expressed some interesting views on the nature and source of Chemical Energy.[1] His argument may be summarized as follows: When 16 grams of oxygen are mixed with 2.016 grams of hydrogen at 0° C, nothing happens, but if a minute spark (supplying a negligible amount of heat) be applied, combination takes place, 18.016 grams of water are formed, and 68,511 calories of heat are given out. Whence comes this relatively enormous amount of heat energy? Suppose we take 16 grams of oxygen and 2.016 grams of hydrogen at —273° C, and add enough heat energy to bring them to 0° C. Dr. Mills shows that the following amount will be needed: For the hydrogen: Raising the temperature from —273° C, 1844.8 calories, supplying heat of fusion and of vaporization, 280.4 calories; total, 2125.2 calories. For the oxygen: Raising the temperature through the same range, 1065.4 calories, supplying heat of fusion and of vaporization, 906.7; total, 1972.2 calories. So that 4097.4 calories would be added to the hydrogen and oxygen in bringing them up from —273° C. to 0° C. Now the energy necessary to raise 18.016 grams of water through the same range of temperature would be 2886.9 calories, divided as follows: For raising the temperature, 1447.4 calories; for supplying heat of fusion, 1439.5 calories. The water at 0° C of course still retains this energy, but since 4097.4 calories were given to the hydrogen and oxygen, and only 2886.9 calories are retained by the water, a balance of 1210.5 calories remains to be given out during combination. *But the amount given out in combination is 68,511 calories, leaving 67,300 calories unaccounted for. Whence comes this energy? In what form did it previously exist?* It was

[1] Transactions Am. Electrochem. Soc., **14**, 35 (1908).

clearly possessed by the hydrogen and oxygen in their solid form at —273° C. Dr. Mills conceives that every atom of a substance possesses at —273° C. a specific chemical energy (though he does not use this term), partly in the potential form, due to "chemical attraction" between it and one or more other atoms, and partly in the kinetic form, which latter condition must be fulfilled if the system of which the atom is a part is to be a stable one.[2] This chemical attraction, or force, or affinity "is probably never directly affected by a rise in temperature,"[3] and the 67,300 calories of energy above mentioned "appears to have been held, intact as it were, neither increased nor diminished, by the changes of temperature, pressure and volume necessary to raise the hydrogen and oxygen to their condition at o° C.," and "represents the total energy change of the three reactions:

$$H_2 = H + H$$
$$\tfrac{1}{2}\, O_2 = \tfrac{1}{2}\,(O + O)$$
$$H + H + O = H_2O$$

when taking place at —273° C."

The reactions liberated this store of energy, but how they did so, and in what form the energy previously existed, Dr. Mills does not attempt to explain. It is possible that some light may be thrown upon this question by a recourse to the electron theory.

The Electrical Theory of Chemical Combination.

It may be well to give first a brief account of some of the fundamental ideas of this theory, as well as of some of its recent developments. It is now a familiar story how the idea of electrons arose. Helmholtz, in his Faraday lecture[4], spoke of electricity being "divided into definite elementary portions which behave like atoms of electricity" in the conduction of a current through a liquid electrolyte. Maxwell had already proposed that "we call this constant molecular charge" (electrolysis) "for convenience of description, one atom of electricity."[5] Lorentz in 1880, in order to explain the phenomena of light, formulated a theory[6]

[2] Meyer, Kinetic Theory of Gases, 2nd English Ed., p. 344.
[3] See also Nernst, Theoretical Chemistry, 4th Eng. Ed., p. 688.
[4] Journal Chemical Soc., 1881, p. 39.
[5] Electricity & Mag., 1st Ed., 1873, p. 312.
[6] Propagation of Light, Wied. Ann., 1880, p. 9.

which regarded an atom of matter as a complex structure consisting of these "atoms of electricity," for which the name "electrons" had been suggested by Stoney, who as early as 1874 had succeeded in calculating the value of the electric charge on one electron. Various theories of the exact structure of an atom out of electrons have been put forth[7], but the most widely accepted view at present is that of Sir J. J. Thomson, who regards an atom as being built up of a sphere of positive electricity of uniform density, throughout which the negative electrons (Thomson prefers to call them "corpuscles") are distributed in various orbits, revolving about the center of the sphere. The number of electrons in an atom is proportional to the atomic weight.[8] The enclosing positive charge acts as though it were concentrated at its center, and is supposed to attract each electron with a force which varies as the direct distance of the electron from the center of the sphere. The "sphere of positive electrification" occupies a vastly greater space than the total volume of all the electrons. These latter, being similarly charged, repel each other according to the inverse square of the distance law.

The electrons are in extremely rapid orbital motion about the center of the atom, the average number of revolutions being about 500 billion per second, and these give rise to light waves. In a neutral atom, the sum of the negative charges on the electrons is exactly equal to the positive charge of the enclosing sphere. In this case the stability of the electron grouping inside the atom depends upon the number of electrons, the way they are arranged in the orbits, and the strength of the enclosing positive charge.

Some atoms easily lose electrons, on account of the instability of their electron groupings. Other atoms have a tendency to acquire electrons from outside, if such increase in number lends greater stability to their electron groupings. The complete solution of the problem of the stability or instability of given electron groupings seems to be beyond the power of mathematics at present, as the electron orbits lie at all angles, but the analytical solution of the case where the orbits of the electrons are supposed to be confined to one plane has been given by Prof. Thomson,[9] and shows

[7] Lodge, Electrons, pp. 148-150.
[8] Thomson, Corpuscular Theory of Matter, p. 164.
[9] Phil. Mag., March, 1904.

that very few groupings of electrons, comparatively speaking, are at all stable. When an atom loses electrons, it thereby loses negative electricity, and a residual positive charge remains. Such an atom would in general belong to an electropositive element. If an atom acquires electrons, its negative charge preponderates over its positive, and the atom acts like an electronegative element. Valency depends on the number of electrons lost or gained. We must not suppose, however, that all the atoms of, let us say, a divalent electropositive element are at any given time in the same condition of having lost two electrons each. In the hurly-burly of atomic and molecular motions and encounters atoms will alternately lose and gain electrons very rapidly, perhaps millions of times per second, but if in the case of the supposed element the atoms have *a tendency to get into the condition represented by the loss of two electrons per atom rather than into any other condition,* the element will have a positive valency of two, and will react with one or more other substances of negative valency as rapidly as the atoms get into the proper condition, owing to the loss or gain of electrons, to go into combination. This requires more or less time, of course, thus agreeing with the facts of chemistry, as no reaction is instantaneous, but proceeds according to an exponential law. *Combination ensues when two or more atoms, carrying unlike charges, and coming near enough for the purpose, are pulled more closely together by the electrostatic lines of force between their charges, and held together tightly in a molecule.* As Ramsay says:[10] "Chemical action is the occasional result of . . . collisions, ... but the process of combination is a comparatively slow one, and . . . . a collision followed by a combination is a comparatively rare event."

With the assumption that chemical affinity is simply electrostatic attraction between charges of electricity, Sir J. J. Thomson has worked out with great ingenuity a series of model atoms, composed of spheres of uniform positive electrification, with varying numbers of electrons revolving in varying numbers of orbits inside these spheres, and has shown that such a series of atoms would show the same properties, periodically recurring, as are actually observed in the elements arranged according to the periodic law.[11]

[10] The Electron as an Element, Journal Chem. Soc., Apr., 1908, p. 777.

[11] Electricity and Matter, p. 117 *et seq.*; Corpuscular Theory of Matter, Chapter XI.

The theory explains more or less satisfactorily the recurring electropositive and electronegative character of the elements, and why the same element acts sometimes electropositively, and at other times electronegatively; the recurrence of corresponding groups of lines in the spectra of elements of the same periodic-law group; the valency of the elements, including the zero valency of the argon group, and also the different valency of the same element under different circumstances; the formation of molecules by the union of atoms of the same element; the existence of unsaturated compounds, such as PCl_3; the formation, in a solution of certain elements (for example, Br and I) of both positive and negative ions, the element appearing at both anode and cathode during electrolysis; the apparent change in the properties of the carbon atom when combined with different elements; the thermoelectric effects, and in fact, nearly all of the phenomena of physics and chemistry. Especially in the explanation of the phenomena of optics and radioactivity has the new theory been of great advantage, and without it the facts of radioactivity, at least, would seem to be entirely inexplicable. Arrhenius has also extended the theory to explain astronomical and metereological phenomena, such as auroras, the solar corona, magnetic storms, etc. But while the electron theory provides us with the broadest working hypothesis of modern times for the correlation and unification of physical, chemical, and biological phenomena, it cannot be claimed that it is in any sense final. One of its founders, indeed, has quite recently pointed out the need for revision or modification of some of its fundamental ideas.[12] Nevertheless, it has already proved to be one of the strongest aids to research which physical science has known.

The Source of Chemical Energy.

Can we obtain, on the electrical theory, any information concerning the source and nature of the energy liberated in chemical reactions? Take the reaction

$$H + O + H = H_2O$$

for example. Before union we have two hydrogen atoms, each

[12] See article by H. A. Lorentz, Phys. Zeitschr., Sept. 1, 1908.

carrying one positive electron charge, and one oxygen atom carrying two negative electron charges. What amount of energy do these charged atoms represent?

The potential of a sphere bearing a charge is equal to Q/r, where Q is the charge on the sphere (in electrostatic units) and r is the radius of the sphere (in centimeters). The resultant potential is given in electrostatic units, an electrostatic unit being equal to 300 volts.

The electron charge has been independently determined by different observers. H. A. Wilson found it to be 3.1×10^{-10} electrostatic units;[13] J. J. Thomson found by another method[14] the value 3.4×10^{-10}. Using the mean value of N (number of molecules in 1 c.c. of a gas under normal conditions of pressure and temperature) given by Meyer,[15] viz., 6.1×10^{19}, we find the corresponding value of the electron charge to be 3.7×10^{-10}.

The value obtained by J. Perrin[16] is 4.1×10^{-10}, and by Rutherford and Geiger[17] is 4.65×10^{-10} electrostatic units.

These last values, being the latest determinations, are probably more correct than former ones. In the following calculation Rutherford's value will be used.

As to the radius of a molecule, estimates vary widely. Meyer gives values ranging from 2×10^{-8} cm. to about 16×10^{-8} cm.,[18] but leans toward the lower figure.[19] The radius of an atom is shrouded in equal doubt, but we may assume 10^{-8} cm. as approximately correct. Using these values we find that the potential, V, of an atom carrying an electron charge is 4.65×10^{-2} E. S. units, or about 14 volts. The energy of a charged body is $\frac{1}{2}QV$ ergs, or, applying our values, the energy of a charged hydrogen atom is $\frac{1}{2} \times 4.65 \times 10^{-10} \times 4.65 \times 10^{-2} = 10.8 \times 10^{-12}$ ergs. The energy of the charged divalent oxygen atom is twice this amount. The energy of the charged atoms entering into combination to form one molecule of water is therefore about 4.3×10^{-11} ergs. Next comes the question of the number of molecules in 1 c.c. of water. This is as

[13] Phil. Mag. [VI], **5**, 429 (1903).
[14] Cond. of Elec. Thro. Gases, 2nd Ed., p. 158.
[15] Kin. Th. of Gases, 2nd Ed., p. 333.
[16] Comptes Rendus, **147**, 594-596 (1908).
[17] Proceedings of the Royal Society, **81** A, 162-73.
Max Planck has calculated the value on theoretical grounds to be 4.69×10^{-10}, and Millikan and Begeman have found it to be, by experimental determination, 4.1×10^{-10}.
[18] *Loc. cit.*, pp. 320, 331.
[19] Perrin gives 2.6×10^{-8} cm. as the diameter of a molecule of oxygen. *Loc. cit.*

uncertain as the values of the electron charge, but it is probably about 3.4×10^{22}. On this estimate the number of molecules in 18 grams of water is 6.2×10^{23}, and the energy of the charged atoms of hydrogen and oxygen would be, before combination, $6.2 \times 10^{23} \times 4.3 \times 10^{-11} = 2.7 \times 10^{13}$ ergs, $= 2.7 \times 10^{6}$ joules, $= 6.4 \times 10^{5}$ calories, or *640,000 calories.* When the charged atoms rush together into combination, this energy, which existed as potential energy of charge, is partly given out, and *it is at least suggestive to note that this amount of energy is sufficient to account for the 67,300 calories given out in the formation of 18.016 grams of water, and is, moreover, of about the magnitude we should expect,* as we do not imagine the atoms to come close enough in combination to release all their energy.

Too much importance, however, must not be given to the number found, 600,000 calories, for the energy of charge of the hydrogen and oxygen atoms may be much greater or much smaller than this. I wish merely to make the point that whatever the potential electrical energy of the hydrogen and oxygen atoms may be before combination, it is less afterwards by the amount given out, *viz.*, 67,300 calories. If the charges on the hydrogen and oxygen atoms "sparked into" each other, *all* of the electrical energy would be given out, but this does not occur.[20] *The hydrogen and oxygen atoms (in a molecule of water) may be considered then as coming quite near each other when in combination, near enough to render the molecule electrically neutral, but not near enough to equalize the charges, and not near enough to prevent stray lines of force from producing a "residual attraction" between the molecules.*

The Residual Attraction.

Dr. Mills in his paper says: "It is possible . . . that the molecular attraction is merely the residual chemical attraction."[21] The electrical theory would simply substitute the word "electrical" for the word "chemical" above. For various reasons Dr. Mills thinks that "the attractive forces . . . which proceed from a particle are definite in amount. If this attraction is exerted upon another particle the amount of the attraction remaining to be

[20] Lodge, Electrons, p. 154.
[21] *Loc. cit.*, p.

exerted upon other particles is diminished." If chemical attraction is electrostatic attraction, we have these conditions exactly fulfilled, and also have an explanation why this force, and the energy due to it, is independent of temperature changes, for the number of "lines of force" proceeding from a given charge is a perfectly definite quantity, unaffected by temperature. The explanation of the "residual attraction" which the electrical theory offers is given by Prof. Thomson as follows:[22] The attraction between charged bodies is greater when these bodies are conductors, in which electrons are able to move about freely, than between non-conductors bearing the same charges, for the conductors allow the corpuscles to move into the most advantageous positions, as it were, and electrostatic induction comes into play. The residual attraction between saturated atoms and molecules will therefore be a function of the mobility of the electrons inside the atoms. "This mobility may not be the same for the atoms of the different elements, and may be different for the same atom according as it is exerting positive or negative valency; in other words, the attraction of an atom may not be wholly exhausted when its valency is satisfied, and the residual attraction may depend not only upon the nature of the atom, but also upon whether it is exerting its positive or negative valencies." The interesting question arises whether this residual attraction is greater or less when an atom carries a positive charge than when the charge is negative. It must be remembered that the theory supposes that the extra electron in a negative monovalent atom is united to a positive atom by lines of force, and that these lines spring from the relatively large surface of the positive atom and converge to the minute electron on the other atom, somewhat as the network of ropes from a balloon converge to the basket beneath. The intensity of the electric field, therefore, at the surfaces of the two atoms is not the same, and we may expect a difference in the residual attraction which an atom exerts when negatively and when positively charged. "In the compound CH_4," says Professor Thomson,[23] "the carbon is supposed to carry a charge of — 4, and in CO (if the oxygen is tetravalent) a charge of + 4; the value of

[22] Corpuscular Theory of Matter, p. 135 *et seq.*

[23] *Loc. cit.*

a[24] for CH_4 is 0.0379, and that for CO is less, viz., 0.0284, although the residual attraction of oxygen is probably greater than that of hydrogen. This, as far as it goes, is in favor of the view that the residual attraction of carbon is greater when it is negatively than when it is positively charged." The residual attraction also appears to exist between molecules, and acts to form aggregates of molecules, especially around negative ions, which seem to exert much more effect than positive ions. "It has been found that in carefully dried gases the velocity of the negative ion is considerably greater than that of the positive when the electrical forces acting on them are equal. If, however, a little water vapor is added to the gas, it produces a considerable diminution of the velocity of the negative ion, while it hardly affects that of the positive. It seems quite possible that this is due to the residual attraction of the OH radicle in the water for a negative charge, making the water molecules attract the negative ions more strongly than they do the positive ones, so that the water molecules will tend to attach themselves to the negative ions, and by loading them up diminish their velocity."[25] Thomson showed years ago that negative electrification had a decidedly greater effect in promoting condensation than positive,[26] and C. T. R. Wilson found that negative ions require less cooling by expansion to make them act as condensation nuclei in dust-free air than positive ions.[27] It is quite probable that these phenomena are explained in the same way. The electrical theory would indicate that there must always be some residual attraction, even in the inactive monatomic gases.

The liquefaction of helium shows this, though for helium the value of a is the smallest known.

Theory of Electrical Conduction.

So far it is significant and interesting to note that the reasoning of the chemist and the physicist, though from different points of view, and expressed in different language, leads to practically the same conclusions. In the case of electrical conduction the differ-

[24] The cohesion factor in Van der Waals' formula.
[25] J. J. Thomson, *Loc. cit.*
[26] Phil. Mag., **36**, 313 (1893).
[27] Phil. Transactions, **193**, 289 (1899).

ence is rather pronounced between Dr. Mills' ideas and those of the electrical theory. Briefly stated, the electrical theory supposes that in metals electrons are easily detached from the atoms, and under the action of an electric force, as when a wire connects the terminals of a voltaic cell, the electrons rapidly pass from atom to atom through the wire in the direction of the positive terminal. This stream of electrons is equivalent to a *positive current flowing in the opposite direction, viz.,* along the wire from the positive to the negative terminal. The kinetic energy of these moving electrons smashing, at it were, into the atoms, causes increased atomic motion, and the wire becomes heated. In the case of metals a rise in temperature retards the motion of the electrons in some way, and the conductivity decreases. In carbon, however, a rise in temperature seems to give the electrons greater freedom of motion, and so the "hot resistance" of a carbon filament is less than the "cold resistance." In the case of non-conductors, like the rare earths, the electrons are only set free by strong heating. In the Nernst glower, for example, conductivity begins only when the temperature is about 1,200° C. The salts of the metals are poor conductors, because the atoms of the metal have already lost electrons, in going into chemical combination, and it is difficult to loosen others and pull them away from the positively charged atoms. In solution, however, the ions of salts are free to move, and we have a double stream of positive and negative ions moving in opposite directions under the electric stress. In gases also there can be no conduction without ionization. In the vacuum tube discharge we have a peculiar case, for we get a stream of *free electrons, unassociated with atoms,* going in one direction, and a stream of positively charged atoms moving in the other. If this latter stream is prevented from reaching the cathode the discharge is stopped.[28]

Dr. Mills' theory of conduction is somewhat ambiguous. He says: "I have in my own mind connected the power to conduct electricity, whether the substance is in the solid, liquid, or gaseous condition, not primarily with molecules, nor with ions, nor even perhaps with electrons. The essential requisite appears to me to be a free, that is, an unabsorbed attraction." It is difficult, on this hypothesis, to see why mercury, for example, should not be a

[28] Lodge, Electrons, p. 39.

better conductor than silver, as its atoms seem to be less firmly bound together; nor why the resistance of selenium should change so marvelously with the degree of illumination to which it is subjected; nor why increase of temperature, which drives atoms further apart, should not always increase conductivity; nor how the vacuum tube discharges and the action of electric valves may be explained; nor how the change of resistance of bismuth in a magnetic field may be accounted for.

However, the object of this paper is merely to emphasize the fact that physicists and chemists, reasoning from different viewpoints, often reach practically the same general conclusions, which is evidence for the truth of these conclusions, and further that the electrical theory, in spite of certain artificial features, seems to offer the best and clearest idea of the source of chemical energy, the mechanism of chemical combination, ionization, dissociation, etc., and the most rational explanation of the various phenomena of physical science.

University of North Carolina,
Chapel Hill, N. C.
February 16, 1909.

DISCUSSION.

DR. G. HINRICHS: The main part of this paper has a somewhat mediæval aspect, being made up of *the sayings* of supposed authorities. All the proposed electrical theories of matter assume the supposed indefiniteness of the ratios of the atomic weights and ignore the fact that fixed, definite and simple ratios have been established by me by a most rigid mathematical analysis of the chemical determinations.

Chemists having, for half a century, blindly accepted the determinations of Stas, have allowed this fundamental subject of the atomic weight to slip from their hands into the control of an international committee. Those of the members of this Society who may wish to study this subject, I respectfully refer to my publications in the Comptes Rendus of the Academy of Sciences of Paris, in the Moniteur Scientifique, and to my

special work. They will, I am confident, become convinced that matter is composed of *one single primary substance,* pantogen, of which I have recently determined the exact atomic weight, and of which the atomic weights of the elements are found to be mathematically exact multiples.

The fusing and boiling points of the elements are obtained respectively from the minimal and maximal moments of inertia determined by the weight and form of the constituent elementary atoms.

Dr. J. E. Mills (*Communicated*): The calculation by Mr. Patterson of the "potential energy of charge" on 16 grams of oxygen and 2.016 grams of hydrogen from the viewpoint of the electron theory is very interesting. While the energy charge so calculated can only be regarded as an estimate, yet it is extremely interesting to note that this estimate amounts to 640,000 calories, and that only 67,300 calories are given out by the three reactions:

$$H_2 = H + H.$$
$$\tfrac{1}{2}O_2 = \tfrac{1}{2}\,(O + O).$$
$$H + H + O = H_2O.$$

This seems to indicate a condition of affairs exactly in accord with the idea that I have already expressed, namely, that the atoms HOH while in the form of water (ice) yet possess a vast amount of energy. I am not in the least surprised that the amount retained should be ten times the amount liberated.

As regards the "residual attraction," I believe that the molecular attraction is probably the residual chemical attraction, being caused by stray lines of force, and while I agree in the main with Mr. Patterson's observations upon the residual attraction, I do not believe that the "electron" theory aids in understanding its mechanism. The number and intensity of these stray lines of molecular force will always be dependent *mutually* upon the atoms which make up the molecule, and no one-sided argument, such as the one quoted from Prof. Thomson, as indicating that the residual attraction of carbon is greater when it is positively than when it is negatively electrified, has the slightest weight. Not only because it is one-sided, considering only the carbon, but because "a" is no measure of the molecular attraction in the sense used.

As regards "electrical conduction," the electron theory considers that electricity is conveyed:

1. In a solution by *ions* moving in *both* directions.
2. In a metallic conductor by *electrons* moving in *one* direction.
3. In a molten salt by *ions* moving in *both* directions.
4. In a gas under ordinary pressure by *ions* moving in *both* directions.
5. In a gas under greatly reduced pressure (vacuum tube discharge) by *electrons* moving in *one* direction and *positively charged atoms* moving in the *other* direction.

I for one will confess frankly that I am not satisfied with a theory of electrical conduction that jumps about at will from electrons to ions, if the usual meaning be attached to those terms. I believe that electricity will be conducted in a gas, in a metal, in a molten salt, and in a solution, in a precisely similar manner so far as the inner mechanism of that conduction is concerned. I attempted in my former paper to state only one of the conditions upon which this conduction depended. I stated: "The essential requisite appears to me to be a free, that is, an unabsorbed attraction." I had no idea of leaving the impression that the conductivity depended only upon this condition. I regarded this condition merely as *one essential factor,* and I discussed this factor alone, because it was this special feature of electrical conductivity that touched the subject I was discussing (chemical energy). I do not pretend to know all of the factors upon which electrical conductivity depends. But to clear up any ambiguity, I would state one other factor: In conducting electricity the *atoms must move.* That is, not only must they have a free, that is, an unabsorbed or indefinitely absorbed, attraction (an attraction which does not bind them definitely to other particular individual atoms), but they must move while they conduct the current.

The electron theory admits the movement of the ions as a necessary part of conduction in a solution, in a molten salt, and in a gas under ordinary pressure. In a gas under reduced pressure it does not wholly deny the movement. But to explain metallic conduction and the vacuum tube discharge, the idea of electrons is introduced. As regards metallic conduction, I would

point out that liquid mercury is a metal and conducts as a metal. Now, if a very large current be passed through the mercury, the motion of the mercury becomes visible and the mercury heaps itself around the electrodes and finally the "pinch" phenomenon is observed. The explanation which has been suggested of this pinch phenomenon as induced by a stress in the ether should not be allowed to conceal the fact that we have here very clear evidence that the atoms of mercury are in motion towards the electrodes. Moreover, we have evidence in every case of metallic conduction that the conduction is accompanied by increased atomic motion, *for the metal becomes heated.* Mr. Patterson says: "The kinetic energy of these moving electrons smashing, as it were, into the atoms, causes increased atomic motion, and the wire becomes heated." Why not drop out the electron clause and confine our attention to the fact that *always,* be it solution, metal, salt, or gas, when a current passes, the atomic motion is disturbed?

My belief that in all electrical conduction the atoms move, is founded not only upon the fact as an independent observation, but is likewise a direct deduction from my statement that the essential requisite of electrical conduction is a free attraction. This "free" attraction is an essential requisite, *because the atoms must move with reference to each other in order to conduct.* So long as the atoms are bound hard and fast to one another and we have no "free" attraction, they cannot move with the freedom necessary to conduct the current, and the body is a non-conductor. And I would again point out what I said before, that the metals are the best conductors *because* they are monatomic; that bismuth, carbon, sulphur, etc., are poorer conductors because their molecules are complex and the atoms are more or less bound to one another; than an oxide, or salt or gas, is a non-conductor just so long as it remains a perfectly definite chemical compound.

Mr. Patterson says: "It is difficult, on this (my) hypothesis, to see why mercury, for example, should not be a better conductor than silver, as its atoms seem to be less firmly bound together; nor why the resistance of selenium should change so marvelously with the degree of illumination to which it is subjected; nor why increase of temperature, which drives atoms further apart, should not always increase conductivity nor how the vacuum tube discharges and the action of electric valves may be

explained; nor how the change of resistance of bismuth in a magnetic field may be accounted for." We would invite Mr. Patterson to give a soul-satisfying explanation of these phenomena in terms of the electron theory.

From my point of view I can calculate the attraction of the atoms of mercury for each other, but the data is lacking for silver, and I cannot therefore compare the molecular attraction of the two metals. But the motion of the atoms, as well as the attraction which also varies with the distance apart of the atoms, are factors to be considered, and I could not, were the attraction known, predict the conductivity.

The change of the resistance of selenium upon exposure to the light, and of bismuth in the magnetic field, are understood by nobody on earth so far as I know. But these changes certainly do indicate a remarkable change in the "phase" of the selenium and bismuth, and it is a well known and legitimate inference that a variation in nearly all the properties of both selenium and bismuth must take place at the same time.

My point of view does not necessitate the conclusion that driving atoms further apart always increases the conductivity. Even if we were to grant that the amount of "free" attraction were thereby increased, we must also remember that the atoms *must move and move further* as they conduct.

As regards the vacuum tube discharge, I had no intention when my paper on chemical energy was written of discussing that phenomenon at all. But I feel now that it is necessary for me to make my position clear. I am a hearty believer in the probable identity of electrical and chemical forces. Or, more clearly expressed, I believe that both electrical and chemical phenomena are caused by a *definite amount of potential energy belonging to an atom.* The part of the electron theory in which I do not at present believe is that this definite amount of potential energy can exist *independently of the atom.* That is to say, I do not believe that the attractive force (electrical or chemical, as you prefer), which I conceive of as proceeding from an atom in all directions, can be rolled into a ball and detached from the atom and exist independently as a corpuscle or electron.

The actual nature of chemical (electrical) energy is a very fundamental question. The nature of mass, of matter, of energy,

and of their relations, must all be considered at the same time. Now, in my paper on chemical energy, after tabulating the main characteristics of the various attractive forces, I expressed the view that any attractive force (f) could be measured by:

$$1.\quad f = \frac{\text{Amount of attraction absorbed at unit distance.} \times \text{Amount of attraction absorbed at unit distance.}}{d^2}$$

Now, the gravitational force (f′) in ordinary terminology is measured by:

$$2.\quad f' = \frac{\text{mass} \times \text{mass}'}{d^2} = \frac{m\ m'}{d^2}$$

and the electrical attractive force (f″) of two electrically charged masses by:

$$3.\quad f'' = \frac{\text{charge} \times \text{charge}'}{d^2} = \frac{e\ e'}{d^2}$$

Now, suppose the gravitational force and the electrical force to be *really identical.* That is, suppose the so-called gravitational, chemical, molecular, electrical and magnetic forces are really only manifestations of one and the same fundamental attraction. Then we have:

$$4.\quad f' = f'' = \frac{m\ m'}{d^2} = \frac{e\ e'}{d^2} \text{ and } \frac{e\ e'}{m\ m'} = \text{constant},$$

a condition which is satisfied if:

$$5.\quad \frac{e}{m} = \text{constant, and } \frac{e'}{m'} = \text{constant.}$$

Thus, from my point of view, I am led to the fundamental discovery of the modern electrical theory, that the ratio of the charge on a body to its mass is a constant. But the interpretation which I must give to this fact is entirely different from the interpretation usually given, for my method of derivation leads me to conclude that the mass of a body varies with the amount of the attraction absorbed at unit distance, and that both mass and charge are relative and not absolute properties. Therefore I do not have to conclude that an electron is a small particle always

with a mass about one thousandth that of a hydrogen atom. I am rather inclined to believe that the hydrogen atom, or any other atom, may itself act as, and become, an electron.

There are at present, even in my own mind, a good many question marks surrounding the above conclusion, and I do not wish to mislead any one. I am at present engaged in revising the papers upon molecular attraction and attractive forces which have lead to this belief, and a complete statement of the reasons for my views will be given in that revised paper.

PROF. A. H. PATTERSON (*Communicated*): I hardly think it necessary to answer Dr. Mills, as my paper is as clear as I can make it in so brief a space. Dr. Mills refuses to admit the existence of electrons independent of atoms, which is, I consider, a demonstrated fact. He further uses as the basis of his whole argument the conception of an "unabsorbed attraction," and I cannot grasp this conception in a definite way. He admits that he cannot at present give it a definite meaning, and also admits that if electrons are proved to exist as separate entities outside of atoms, his theory is practically shattered. That is the crux of the situation as between his theory and the electron theory.

A paper presented at the Fifteenth General Meeting of the American Electrochemical Society, at Niagara Falls, Canada, May 8, 1909; President E. G. Acheson in the Chair.

THE USE OF BAKELITE FOR ELECTRICAL AND ELECTROCHEMICAL PURPOSES.

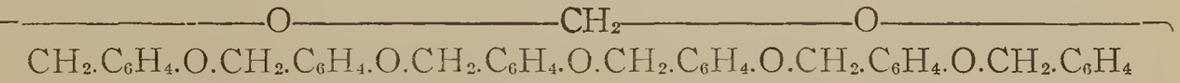
By L. H. Baekeland, Sc. D.

In my first paper on Bakelite read before the American Chemical Society,[1], I have set forth the theoretical reasons why we may consider Bakelite C., or the final product, as a polymerized compound anhydride of a phenol-alcohol and methylenglycol.

I have explained then and there how I have succeeded in producing this compound through indirect synthesis by the action of oxybenzyl alcohol on formaldehyde as well as by direct action of phenols on formaldehyde. The latter method is the more available one for practical purposes, and consists in heating under proper conditions, a mixture of phenols and formaldehyde in presence of a catalytic agent, preferably small amounts of bases or alkaline substances. According to the conditions of operating, I have succeeded in carrying out the process in three phases, designated as A, B and C.

A is the "initial product of condensation" produced by elimination of water, and contains probably one or more hydroxyl groups in its molecule.

B is the so-called "intermediate condensation product," a higher anhydride evolved by further elimination of water. In the case of ordinary phenol, we then have oxybenzyl-methylenglycol anhydride, the formula of which may be represented as



C is the polymer of B and can be represented by:

$$n(C_{43}H_{38}O_7)$$

[1] See Journal Indust. & Eng. Chemistry, March, 1909, 149; Electrochem. & Met. Ind., March, 1909, 111.

or its homologs in case the other members of the phenol series be used.

It is the final condition in the Bakelite process. This product C is characterized by the following properties:

It is a hard structureless mass, which may be prepared in transparent or in opaque condition; its color varies from that of colorless glass to amber color or dark ruby or brown. It is harder than shellac, hard-rubber or celluloid, but misses the flexibility of the two latter substances and this is its main defect. On the other hand it withstands all solvents and most chemicals, resists boiling water, steam and superheated steam and oils. Heating does not melt it, nor even soften it to any serious extent. Boiling concentrated sulphuric acid destroys it; so does concentrated nitric acid, but it withstands dilute sulphuric acid, hydrochloric acid and chlorine. It can stand temperatures of 300° C. and over. At the temperature of melting glass it chars and carbonizes without entering into fusion. In its final condition it can be sawed, cut, bored and turned on the lathe, but it can no longer be molded for practical purposes. In other words, when it has acquired condition C it is no longer a true plastic, so that all operations of molding or shaping must preferably be carried out in its earlier stages. In its final stage it is tasteless and odorless and an excellent insulator of heat and electricity.

In cost of production it can very advantageously compete with any known plastic.

For all practical purposes we use A as raw material to start with. The latter is obtained in four varieties, each of which may be preferable according to the special purpose in view.

Extra thin liquid A is a thin liquid of great penetrating power, and therefore is best fit for impregnating such bodies which absorb liquids with some difficulty, as for instance wood.

Liquid A is another variety of which the consistency is about that of molasses syrup. It can be made considerably thinner by slight heating. Longer heating at 60° to 70° C. thickens it gradually so that it can become pasty; still longer heating at this temperature may convert it into B, which is no longer fusible, but still remains soft while hot.

Dissolved A is a mixture of A with a small amount of alcohol which can be further diluted to proper strength by the proper

addition of alcohol. If an excess of alcohol be added to it, the whole dissolved mass may reprecipitate and separate itself in two layers: a lower viscous one, containing the precipitated A, and a supernatant thin liquid containing mainly the added alcohol. Acetone redissolves this precipitate. The alcoholic solution dries in about the same way as shellac varnish, but drying at ordinary temperatures or even somewhat higher temperatures, does not bring the layer beyond the stage A, in other words this varnish layer remains fusible and soluble. Only at relatively high temperatures and in presence of suitable amounts of catalytic agents does it transform finally in hard, insoluble C. In all cases where the coating is rather thick or where it is applied on porous surfaces like wood it becomes absolutely essential to carry out the heating in a Bakelizer under suitable pressure as explained below so as to avoid air bubbles and blistering.

Solid A. A brittle irregular, opaque, translucent or transparent mass of about the consistency and brittleness of ordinary rosin or colophonium. It can be made in degrees of hardness ranging from a variety which melts at 40° C. or under, to a modification which melts only at 100° C. or over. If heated for a few hours at about 70° C., it slowly hardens more and more, then changes into B. The main characteristic of Solid A is that it still is fusible and soluble in caustic soda as well as in acetone or in a mixture of alcohol and acetone.

It can be easily ground to a fine powder and mixed with any variety of fillers and thus become very well suited for the manufacture of molded objects.

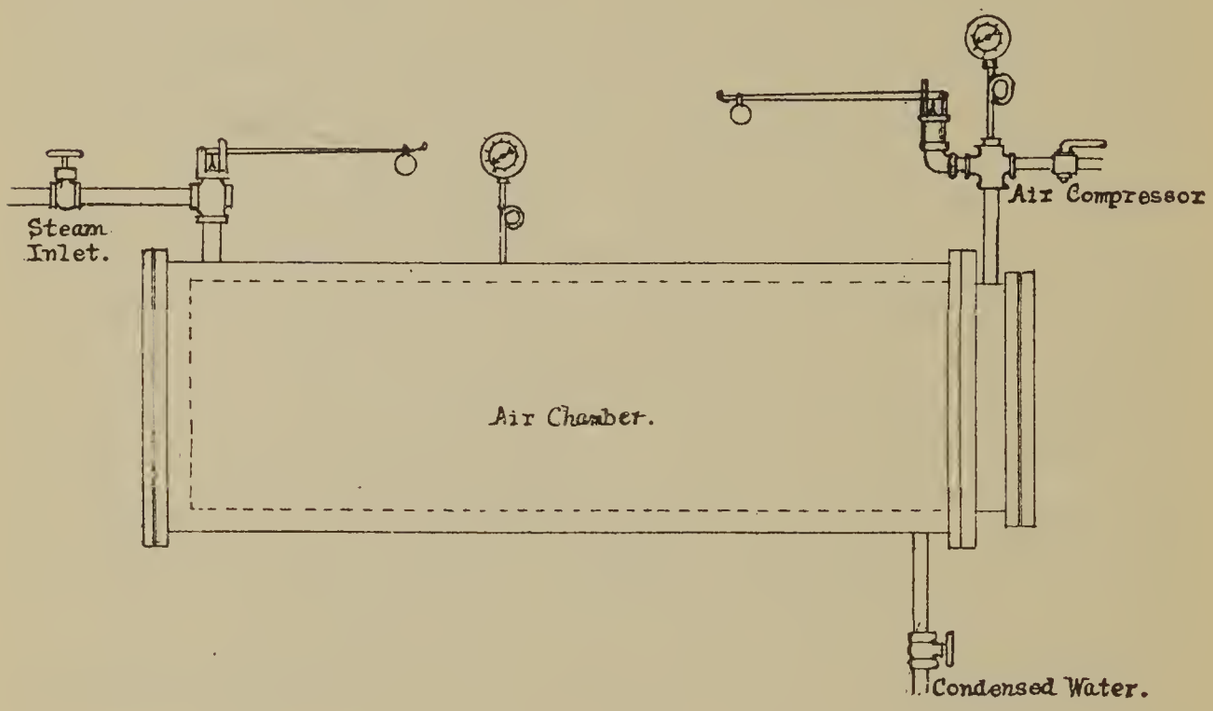
Solid A at first sight resembles very closely B; it has the same appearance, is about of equal brittleness, but B. if heated does no longer melt, although it softens and becomes rubber-like. Furthermore, B is insoluble in neutral solvents; acetone and phenol may swell it somewhat, but not dissolve it. How the valuable properties of A are utilized in practice, we shall see later on.

In the different modifications of the Bakelite process the aim in view is to produce the final product C; but in as far as C is no longer plastic, all forming, shaping, molding or mixing is carried out in the earlier stages.

This is accomplished either by transforming directly A into

C in one single operation, or in other cases, specially in rapid molding processes, it is found more convenient to change A into B, then remove B from the mold, and afterwards change it into C without the use of a mold. In some other case the molding or shaping process is started from B and the latter is then changed into C by the application of heat.

Whether stage C is arrived at directly from A or indirectly from B, the quickest result and the best product is obtained by heating at relatively high temperatures, say 160° C. or over. But as at temperatures above 100° C., A dissociates into gaseous



BAKELIZER.

products and causes the resulting mass to be porous and spongy, I found it necessary to heat under pressure. Without this precaution the resulting mass will be technically worthless.

If the heating occurs in closed molds or closed vessels the so developed internal pressure may be sufficient to counteract the chemical dissociation which causes porosity.

In all other cases the heating should be conducted in a so-called Bakelizer as shown by sketch:

This is an apparatus consisting essentially of an inner chamber where the objects are placed and in which, by means of a suitable pump, air can be compressed to 100 or 120 pounds; this pressure is maintained during the heating. A steam-jacket heats the

chamber to a temperature of 140° to 180° C., equivalent to from 54 pounds to 150 pounds of steam.

The higher the temperature, the shorter will be the Bakelizing process, which converts everything into C.

In such cases where Bakelite is used in presence of substances which can not stand such high temperatures, as for instance, wood, wood-pulp or paper, somewhat lower temperatures should be used and the operation takes more time. All these conditions have to be adjusted after direct experiment for each different material. For substances like asbestos or other mineral fillers it does not matter if temperatures as high as 200° C. and very long Bakelizing be used.

The different applications of Bakelite can be divided summarily into block-working processes, impregnating processes, coating processes and molding processes.

In some cases one or more of these processes are carried out conjunctively.

Block-working. This process suggests itself naturally to the mind and can be carried out in many ways. The simplest manner is to heat a mixture of phenols and formaldehyde under pressure in presence of a condensing or catalytic agent, say a small amount of a base. But it is more advantageous to start with one of the varieties of A described above. The A may be simply poured in a mold or mixed first with pigments, colors or suitable filling materials, for instance, asbestos, clay, mica, bone black, iron oxide, saw dust, wood pulp, finely divided metals, mica, abrasives, graphite, etc., and thus produce an endless variety of compositions more or less suitable for certain special purposes. By heating the mass at 140°-180° C. under suitably increased pressure, the whole solidifies to a solid block, which has the exact shape of the container and can easily be removed therefrom because there is a slight shrinkage. The process may take from one to two or three hours according to the size of the block, the temperature and the amount of base used. If organic fillers are used which are destroyed by too high temperatures, as for instance, wood-pulp, then the minimum temperatures must be preferred and the time of heating must be increased accordingly. No such restrictions exist for mineral fillers.

The so-obtained blocks can now be sawed, cut, turned, polished and shaped in about the same way as ivory or bone is handled.

For large blocks the following difficulty presents itself: In the final act of polymerization, the mass contracts in volume, and as it is rather difficult to carry out the heating in a sufficiently gradual manner it may happen that the crust be transformed in C before the heat has made its full action felt in the center. This may cause rents or cracks through the mass. Furthermore, C is very hard, and difficult to cut, saw or turn. Therefore, it is easier to simply continue the heating until stage B is reached and then cut the latter to the proper shape; then B is submitted to further action of heat until it is changed into C.

I should mention that B while slightly warm is soft and somewhat elastic and cuts about as easily as Swiss cheese, yet if heated further it does not liquefy nor change its original shape. The transformation of A into B does not need to be carried out under pressure. It may be accomplished simply by heating for a few hours, at temperatures not exceeding 70° C., any of the varieties of A, either in an air stove or in a water bath. The progress of the reaction can be easily followed by the touch. The A will thicken more and more until it is no longer fusible and feels elastic in about the same way as coagulated gelatine. When this stage is reached, B can be removed from its receptacle and be cut to proper shape, or the block can simply be cooled and stored away for future purposes. On cooling, B becomes hard and brittle, but if dipped in hot water it becomes soft again and regains its former elasticity.

In order to change B into C it can be heated to proper temperature in a Bakelizer as described above. B is no longer attacked by hot water, as A is, and for that reason it may be simply heated in an ordinary autoclave containing water, in about the same way as rubber is vulcanized for dental purposes, with this difference, however, that higher temperatures should be used than are permissible in the rubber process.

Molds are here entirely superfluous and the objects so treated will retain perfectly their shape. Temperatures of 160° C. to 170° C. are quite suitable, but I have used with impunity temperatures as high as 200° C. and over.

I mention this fact for persons who are acquainted with rub-

ber vulcanizing and who are inclined to carry out Bakelizing at too low temperatures or too short a time; indeed, "over-vulcanizing" is a constant menace to the rubber manufacturer.

Plates, blocks and objects of various sizes and dimensions may thus be manufactured easily, but this process, however simple, does not commend itself in such cases where large quantities of articles of the same size have to be produced. For such purposes it is much cheaper to mold in the press, which allows quick and accurate work, without further necessity of milling or machinery or polishing. How this is done is described under the heading of molding processes.

Impregnating processes: Liquid A, specially in its extra thin variety, is readily absorbed by any porous materials. Its penetrating power is far superior in this respect to varnish solutions, rubber solutions, or similar viscous or incompletely dissolved masses which have a tendency to merely stay on the surface notwithstanding the aid of high pressure.

If a piece of non-resinous soft wood, like bass wood or poplar wood, be immersed in extra thin liquid A, after a few hours it will be found that the wood has doubled or even tripled its former weight. The absorption of the liquid is accompanied by some swelling of the wood and the latter becomes translucent on the edges, which shows that the interior of the individual wood-fibers is entirely filled. The same treatment can be given to unsized paper, paper pulp, cardboard, asbestos, objects of cement or plaster of Paris, in fact, to any material of a fibrous, cellular, or otherwise porous texture.

For such articles which absorb easily, regular liquid A can be used, although it is somewhat thicker; in this instance slight heating will render it more fluid. In other cases it becomes necessary to use extra thin liquid on account of its greater penetrating power. The addition of solvents like alcohol or others does not work well except in special cases, as for instance, thin sheets of blotting paper, because these solutions do not seem to penetrate as well; furthermore the use of solvents introduces a new factor which retards the synthesis.

Resinous woods like pine are very difficult to impregnate. Bass, poplar and similar woods, as well as unsized pulp board are easily impregnated by plain soaking, and this can be helped

by the usual methods of injection under pressure. The preliminary use of a vacuum does not seem to be so advantageous from the fact that when liquid A enters the vacuum chamber it dissociates, evolving formaldehyde gas and the liquid starts boiling and foaming violently. I found it much simpler to heat the substance that has to be impregnated at about 120° C. for several hours until all water and air is expelled and then to immerse the objects, while they are still hot, into the liquid A, where they are left to soak; if more complete impregnation is desired, the force pump may be resorted to.

The impregnated material is now transferred to the Bakelizer and submitted there to final treatment.

It should be borne in mind that we have to deal here with chemical phenomena occurring in capillary spaces. Under the latter conditions chemical reactions are considerably retarded. The chemical dynamics here are much influenced by decreased mobility of the reacting molecules. For this reason it is necessary to heat longer than for ordinary conditions.

On the other hand, the capillary conditions depress at the same time, the tension of dissociation; this explains why wood or cement impregnated with liquid A can be heated at temperatures somewhat above 100° C., without applying pressure and yet not give a porous result. So under these special conditions a Bakelizer can be dispensed with by raising slowly the temperature from 70° C. to 130° C. But even then we have to guard against a considerable loss of formaldehyde vapors which are set free during the first period of heating and which may prove a disturbing factor by altering too much the chemical composition of the impregnating material.

So that, after all, whenever heating in a Bakelizer is practicable, it ought to be preferred even if only for the fact that it will shorten the heating process very considerably.

It is advisable to supplement the treatment with a slow afterdrying so as to expel any traces of water which may have been liberated during the synthesis.

In most instances it will be found that the impregnated objects have a dull appearance on the surface. Whether this be due to the fact that the pressure in the Bakelizer has forced the liquid inwards, or whether it has to be ascribed to surface evaporation,

it can be easily remedied by applying a second superficial coat of thicker A.

The latter is best applied while the objects are still hot; this treatment will impart a very hard and very glossy surface.

Wood thus treated is not only much harder and stronger, but it has become rot proof, and is a better electrical insulator. It withstands dilute acid solutions and ordinary electrolytes. It can be used to excellent advantage for third-rail covers. Similar usages can be found for impregnated pulp board, cardboard and asbestos board.

Asbestos paper or asbestos tissue impregnated with A or B, makes an excellent packing material for gaskets, washers and similar purposes.

In that condition it can be carried in stock indefinitely, either in the form of flat sheets or in ready-made sizes. As soon as this packing material is applied to a hot surface under pressure, the A becomes plastic and molds itself thoroughly over the surface and is gradually transformed into hard permanent C.

In certain cases, the admixture of graphite or similar filling materials may prove advantageous.

The impregnation of coils for dynamos, motors and transformers: Bakelite gives us a ready means to provide these apparatus with a hard and strong insulating mass which cannot soften under the influence of heat, and withstands temperatures at which all hitherto used gums or resins would melt away. Every electrical engineer knows what this means in relation to running "overloads."

But the use of Bakelite for these purposes involves new questions in the technique of impregnation: It should not be forgotten that by the synthesis of Bakelite, a certain amount of water is set free and this water must be eliminated from the coils by after drying. Furthermore, Bakelite in its final state C, although very hard and tough is not flexible; so that any wires or conductors coated with it can no longer stand much bending or twisting, and for such parts, the Bakelizing operation should only take place after all wires and conductors are in their final place.

With this aim in view, the wire or conductor, provided with its covering of cotton or asbestos can be simply coated with dissolved A, the solution properly diluted with the necessary amount

of alcohol, then submitted to spontaneous drying. This may be helped by a gentle application of heat, but never more than is necessary to carry the material to the stage B, so as to maintain the necessary flexibility. The wire is now wound as usual, and in order to insure more flexibility it may be found useful to heat it slightly. Tape or any fabric, or asbestos impregnated with A, may be put between successive layers, just as is done when shellac is used as an insulator; after the coil is made up it is now introduced in the Bakelizer.

In case the wires are covered exclusively with asbestos it will be advantageous to heat the Bakelizer at highest temperatures; however, if cotton or similar organic materials be present, such high temperatures would destroy and carbonize them and it may be safer not to exceed 140° C. After Bakelizing, the coils should be submitted to slow drying so as to expel any remaining traces of moisture or solvents, and this operation can be hastened considerably by the use of a vacuum dryer.

In other cases ready-wound coils may be simply impregnated with liquid A, using the precautions as described for the impregnation of wood. Capillary conditions as described for the wood impregnating process exist here; so that, with some precaution it is possible to slowly transform A into C or at least into B, in an ordinary drying stove, without the absolute necessity of resorting to a Bakelizer; always, provided the heating be started at temperatures as low as 60° to 70° C. and gradually increased to 120° to 140° C.

In fact it may be found sufficient not to go beyond B and leave it to future self-heating of the wire when run under overload to arrive at the final condition C.

It ought to be mentioned here that in such coils with many layers of metallic wire, the outer shell of B may act as an envelope which insures internal pressure during the heating process, just as if it was in a closed vessel, and thus prevents dissociation and the resulting formation of a porous mass.

As a modification to above methods, I should suggest the following:

The coil after being properly impregnated may simply be put in an accurately made closed mold and the latter may be filled with more A, using pressure if required, so that after Bake-

lizing it the whole will come out in accurate size and shape and present a much neater appearance than the ordinary clumsy coils now in use for dynamo and motor construction. The very fact that henceforth it is possible to mold coils in regular shapes and most accurate dimensions, may ultimately simplify the construction of this class of machinery and render renewals much easier.

Coating processes: The simplest way for coating an object with Bakelite is to dip it in liquid A and then finish it in the Bakelizer. By slightly heating the objects and by using rather thick A, the operation becomes rather simple, especially for metallic objects. Or the A coated objects may be first heated gently in a stove until the A has been transformed in B and then the object may be transferred to the Bakelizer. Several coats may thus be applied in succession until any desired thickness is attained. This method of building up a thick coat by several layers takes away the danger of cracking or splitting when thick coats are applied all at once.

The sudden contraction during polymerization has to be taken into consideration here. There is another way of counteracting the effect of too much contraction, namely the incorporation of suitable filling materials as silica, or fine sand, clay, slate dust, powdered asbestos, etc. Any of these materials added to liquid A in suitable proportion will give a putty-like mass which can be easily kneaded, specially if slightly heated; it can be applied and modelled to any kind of surface to the desired thickness and shape. This same mass can be rolled out in thin sheets and the latter can be applied on the inside and outside of metallic vessels. The whole can be directly finished in the Bakelizer or be heated previously at low temperatures so as to bring it first in B state. This method gives a ready means for covering iron pipe or pumps or similar objects with a layer of protective material and thus render them more suitable for chemical engineering purposes. Thick layers of Bakelite without filler, or mixtures containing little filler do not adhere well to metallic surfaces. But by using more filler and specially by using gritty materials as fillers, like sand or abrasives, the adherence becomes excellent. For instance, mixtures of emery with about 10 to 15 per cent. liquid A, can be made so that after Bakelizing they will stick to

glass to the point that they can no longer be removed unless by chipping off pieces of the glass.

A composite coating of Bakelite can also be applied on wooden or metallic vessels by first dipping a sheet of asbestos in A, partially transform it into B by heating, then stick it, by means of thick A, to the surface which is intended to be protected, and afterwards press it against the surface by means of a hot, smooth plate. The latter operation is finished in about ten or fifteen minutes if the pressing plate is maintained sufficiently hot. By selecting polished metallic pressing plates, a very beautiful finish can be obtained at the same time. In this case Bakelite not only acts as impregnating and finishing material, but also as an excellent and permanent adhesive.

A modification of this method has given splendid results for veneering and finishing wood, accomplishing in a few minutes results which heretofore could not be obtained after weeks of polishing, sandpapering and revarnishing with the older methods as practiced by piano and furniture manufacturers.

A similar method may become useful for lining wooden or metallic boxes with impregnated asbestos so as to make them suitable for electrolyzing tanks or storage batteries.

Whenever very thin layers of Bakelite have to be applied, it is found simpler to use A in alcoholic solution as a varnish; for this purpose, dissolved A, properly diluted with three to four times its volume of wood alcohol, is very suitable. This can be done by brushing, dipping or spraying. This varnish dries in a few minutes to the point where it is no longer sticky, but it may take several hours before it is entirely dry. Even then the last traces of solvent are not expelled entirely, and even after years the layer remains A, soluble and fusible. If temperatures above 100° C. are applied, we may get nearer the stage C, but there is a decided tendency towards blistering, especially in such spots where the varnish has been applied rather thickly.

The use of the Bakelizer prevents all this, and for wood or other materials which have a porous surface it is entirely indispensable. For metallic surfaces, by using great precaution and thin layers, and by raising the temperature very gradually until it attains 120° to 140° C., a hard coating may ultimately be obtained.

Sheet iron, or stamped boxes provided with a thin coating of Bakelite, can stand boiling dilute sulphuric acids and boiling neutral solvents.

It should be borne in mind that on account of the limited flexibility of Bakelite, such sheets can not be twisted or bent beyond certain limits without splitting the protective layer. In any such cases where bending has to be done, it must be made before the varnish is applied or after the A has been changed in B, which still leaves some scope for flexibility.

Molding Processes: The simplest but slowest way for molding Bakelite is to pour liquid A, alone or mixed with fillers, in suitable molds and heat in a Bakelizer. This operation may take as much as one to three hours, according to the temperature or the size of the object; so that this process has the objection of requiring the relatively long use of molds. It can be shortened by simply carrying the heating process until the B stage, after which the objects can be expelled from the molds and finished in the Bakelizer at any suitable time thereafter and without the further use of molds. The B stage can be obtained by plain but slow heating in a stove or water bath, or by rapid heating in the Bakelizer. But even all this is too slow for many purposes where quick and accurate molding is essential. It then becomes simpler to mold in a hot press. For this purpose a hydraulic press, or a screw press, or even a lever press can be used, as long as it is provided with contrivances whereby the plateens can be heated and cooled quickly, either by steam and cold water circulation, or by gas heating. Temperatures as high as 200° C. are desirable for rapid and best work, but the molding can be done also at 80 lbs. steam pressure. It is a noteworthy fact that molds under high pressure contact with the plateen, heat up and cool quicker than if not under pressure.

I tried first mixtures of liquid A with various filling materials, the mass being mixed between rollers same as are used in the rubber industry, but I found afterwards that this slow and expensive method of mixing is entirely necessary if solid A be used.

Furthermore, liquid A has the disadvantage over solid A of requiring a longer time for molding. Solid A has the great advantage over other plastics in that the first action of heat

liquefies it entirely so that high pressures, as required for molding celluloid, rubber or resinous materials, are superfluous unless large amounts of filling materials be used which make the mass less plastic. After the first liquefying action of the heat, the immediate after-effect is quite contrary; namely, the hardening of the mass while A becomes B, then C. The main function of the pressure in the act of molding A is to counteract the dissociation which would cause porosity and resulting lack of homogeneity. This explains why astonishingly accurate molding —for instance, talking machine records—can be made with Bakelite under low pressure, provided sufficient heat be used. Persons who are familiar with the molding of celluloid, shellac or rubber compositions, when trying Bakelite for the first time are apt to heat the molds insufficiently, being under the wrong impression that high temperatures may spoil Bakelite in the same way as the compounds to which they are accustomed.

The great penetrating power of A makes it possible of making molded objects containing as little as 10 per cent. and even less of Bakelite, the remainder being made up of suitable fillers, for instance, asbestos.

Quantities of 20 to 30 per cent. of solid A and 80 to 70 per cent. of asbestos make excellent compositions for molded insulators.

In some cases it may be found desirable to increase the amount to about 40 per cent. Wood pulp or ground sawdust require these larger proportions if the objects have to stand boiling water without losing their gloss.

The mixing of these compounds is very simple work. The solid A is pulverized in a porcelain ball mill and ground to 50 or 100 mesh. If trouble is experienced on account of the ground material sticking to the walls of the mill, this can be easily obviated by adding about 10 per cent. of the filler, which prevents "caking." The so ground A can be kept in reserve for further use. It is then mixed in suitable proportions with the finely powdered filling materials and reground in a ball mill so as to insure thorough mixing. This mixed powder is now ready for molding; on account of its bulkiness it may be found preferable to compact it somewhat by pressing it slightly or rolling it into sheets while being gently heated. The resulting sheets

or cakes can be kept in stock. To use these for molding they are put into the slightly heated molds, and the latter are pressed now between the very hot plateens of the press, which squirts out any excess of material. Pressing and heating is continued until the A is transformed into B, after which the molds can be emptied. According to the size of the molded objects or the temperature, molding is finished in a time varying from twenty-five minutes to three minutes, and even less for small objects.

Molded objects of Bakelite in B condition are about as strong as shellac, but they still soften under the influence of heat. They become considerably stronger and acquire their final resisting qualities by being heated in the Bakelizer. This final treatment can be carried out at any suitable time, all the pieces being put in together. No molds are needed here because B, although soft while hot, does not melt any longer, and keeps its shape while submitted to the high heat of the Bakelizer.

We here observe again a slight shrinkage of volume, which has to be taken into consideration while designing the molds. This contraction is always the same for the same compositions, and becomes very small if large amounts of fillers are used. By taking these factors into consideration the molding can be done with an accuracy of 0.001 inch or better.

We have stated above that C can not be molded; it is no longer a plastic, in other terms, its particles if pressed together do not give a strong coherent mass where all the particles are welded homogeneously together.

On the other hand, B, although infusible and insoluble, softens when heated under high pressure and welds and molds together.

This enables us to still further simplify the molding operation by using ground B instead of A. But it then becomes necessary to use maximum temperatures and highest possible pressure, B not flowing so easily as A. This is specially indispensable when large amounts of filling material are employed. This method of working is decidedly advantageous when a highly polished surface and very accurate molding is desired. By keeping long enough in the mold, no after-treatment in the Bakelizer is required, and the gloss imparted by a polished mold

is thus kept intact. The use of B is also advisable in such instances where mixtures rich in Bakelite are desired. Whenever mixtures are made containing over 40 or 50 per cent. of A there is constant danger that during the act of molding the A may ooze out before it has had time to be changed into B. By using directly B this difficulty no longer exists and there is no further limit to the quantities which may be employed in a molding mixture.

For such molded electric insulators which are expected to stand high temperatures, finely ground asbestos, clay, mica or other similar mineral fillers should be used. If temperature specifications are not so important, then organic fillers like wood-pulp or ground sawdust are available and give nicely molding compositions of which the insulating coefficient is frequently considerably higher than that of asbestos. Some varieties of Canadian asbestos prove to be much less desirable for high voltage insulation; this is probably due to mineral impurities and to the higher content in water. These differences in insulating properties do not play much importance for voltages below 40,000. On the other hand, asbestos, on account of its fibrous texture, lends great strength to Bakelite compositions and makes them stand better the shattering effect of direct impact or concussion.

The difference in insulating properties of asbestos is clearly shown by comparing results with a sheet of blotting paper impregnated with Bakelite and of asbestos paper of the same thickness, treated in the same way. The impregnated blotting paper may puncture at voltages two and three times higher than the asbestos sheet.

Bakelite compositions lend themselves more or less to kneading, filing and sawing, according to the nature of the filler. In this direction, compositions containing fibrous materials show again the best results.

I have stated before that Bakelite alone can stand 300° C., but compounds which contain large amounts of mineral filler may be made to stand even higher temperatures. Those con-

taining wood-pulp, sawdust or other organic fillers will stand less, the filling material being destroyed before Bakelite.

It is a well known fact that whenever rubber is used as an insulator it slowly emits sulphur vapors, which by and by attack metallic parts and may cause serious injury to delicate copper wires or metallic connections. Bakelite, not emitting any such objectionable emanations, does not possess this defect, and therefore has been preferred in the manufacture of delicate electrical instruments.

But I have not yet mentioned another advantage of Bakelite insulators over those made of shellac or other resinous materials.

It is a known chemical fact that the latter are all apt to hydrolize by the action of water or dilute alkalies. This action is readily shown whenever water is dripped on a table varnished with shellac, which causes whitening on the wet spots. This effect is more pronounced whenever a small amount of ammonia is present. A similar action occurs whenever the conditions of the atmosphere deposit a thin film of moisture on shellac insulators, so much the more as the air always contains traces of ammonia. This superficial hydrolysis which forms on the surface of resinous insulators a thin film of conductive, chemically changed resin, may explain the so-called "creeping" of high voltage currents along the surface of resinous insulators. The very fact that Bakelite can be heated in presence of water and ammonia in an autoclave at 200° and over without hydrolysis, makes us feel safe as to its resisting power to atmospheric influences.

Whether Bakelite-asbestos or Bakelite-mica insulators will answer the purpose for high voltage insulation as well or worse than porcelain is a matter which experience and the test of time alone can decide.

For insulation in third-rail systems, where continuous vibration of passing trains plays havoc with brittle and unreliable porcelain, Bakelite-asbestos has indicated decided superiority after several months of continuous service, as well as by direct laboratory tests; besides greater strength, it has shown more regularity in manufacture and allows more accurate molding, which permits closer designs and smaller margin of safety.

There is no difficulty whatever in imbedding metallic parts, like bolts, cores, screws, washers or reinforcing members in the molded mass.

In the following table are condensed some comparative results which have been communicated to me by users of Bakelite who previously had acquired great skill in the manufacture of other excellent insulating compounds, and by this fact were better able to draw comparisons.

Electrical Tests.

No.	Name of Piece	Bakelite	Remarks
1	Spool	Punctured at 16,000 to 18,000 volts	Asbestos hard-rubber composition punctured at 4,000 to 8,000 volts.
2	Square Tube (hollow) thickness, .103″	Punctured at 21,000 volts	Asbestos hard-rubber composition punctured at 17,000 volts.
3	Washer thickness, .062″	Punctured at 20,000 volts	Asbestos hard-rubber composition punctured at 11,000 volts.
4	Discs of various compositions. thickness, .0625″	Punctured at 45,000 volts	These tests are still unfinished and were made on various Bakelite compositions.
	" .162″	" " 31,000 "	None on pure Bakelite.
	" .165″	" " 22,000 "	
	" .375″	" " 42,000 "	
5	Disc thickness, .095″	" " 18,000 "	Asbestos hard-rubber composition punctured at 1,500 volts.
6	Cup Insulator thickness, .375″	" " 42,500 "	
7	Line Insulator	Arc to pin, dry at 50,000 volts	Used on 11,500 volt line.
8	Rail Insulator	Resistance *dry*: 5,625 megohms	Porcelain resistance *dry*, 4,550 megohms.
		Resistance *wet*: 0.5 to 65 megohms (These tests are only approximate in megohms.)	*wet*, 0.2 to 10 megohms.
		Arc over hook bolt to rail 27,000 volts	Porcelain arc over 26,400 volts.

Mechanical Strength Tests.

No.	Name of Piece	Bakelite	Remarks
2	Square Tube (hollow) thickness, 103″	Traverse strength, 6 inch centers, 1,850 pounds	Asbestos hard-rubber composition 1,700 pounds.
8	Rail Insulator	Ultimate strength compression, 96,000 to 110,000 pounds	Porcelain 45,000 to 85,000 pounds.
		Ultimate strength tension, 3,200 to 5,500 pounds	Porcelain 1,400 to 2,300 pounds.
		Impact test, no limit found for same blow as porcelain was submitted to.	Porcelain 38 to 100 blows.
9	Cup Piece, hollow cylinder 3″ high, 1¾″ diameter, .045″ thick	Ultimate compressive strength 2,550 pounds.	Loaded on top.

Heat Tests.

10	Valve Interior	At 265 pounds, steam about 460° Fah. for one hour.	No effect on the composition.
11	Packing Nut Graphite composition	Tight at 65 pounds, steam 200 r. p. m.	Could turn 3 inch shaft by hand.

Note.—All of the Bakelite Insulation shows an unusual uniform resistance at varying temperatures from 0° to 300° Centigrade and does not soften at much higher temperatures. Most of the insulation contained about ⅓ Bakelite and ⅔ finely divided asbestos.

Before leaving this subject mention should be made of the properties of special mixture of Bakelite with graphite, of which I have here some specimens. Both these materials compound very well together in almost any proportions. Liquid A or solid A can be used for this purpose. By varying the amounts of Bakelite, these compositions may be made of varying hardness, from such ones as write on paper like the softest pencils, to others which are so hard that they no longer leave a tracing when rubbed against a ruguous surface. I do not know in how

far this may be utilized in the pencil industry, but I have obtained some very encouraging results by trying to use them for self-lubricating bearings. The fact that such bearings can be molded very accurately at little cost makes their interchangeability and rapid renewal a very easy matter. Dynamos or motors or other rapid revolving machinery, where lubrication is a delicate matter, might be provided with such bearings instead of the older metallic bearings. Bakelite-graphite bearings will not melt nor soften in case of overheating; they can be used in conjunction with oil like any other bearing, and in case of insufficient supply of oil the graphite present will supply the necessary lubricant.

As a lining for pumps which are required to handle liquids which corrode iron, the same mass may find its uses.

But Bakelite-graphite composition presents other possibilities from an electrical standpoint. It namely gives us a means of producing a material of which the electrical resistance can be changed at will in a very wide range by changing the proportion of Bakelite.

Finally, I might mention that I have tried to decrease the porosity of graphite anodes in electrolytic cells by the injection of extra thin liquid A, and Bakelizing afterwards, but although in a first experiment we were able to decidedly decrease anode corrosion, I am not yet sure whether this was due to direct action or to a somewhat lessened conductivity. This may be a suggestion for Dr. Turrentine in his experiments with graphite as electrodes for electrolytic analysis.

DISCUSSION.

MR. K. B. MILLETT: Dr. Baekeland, did you say that this Bakelite is rather brittle? If you treat wood with Bakelite, can a nail be driven in the wood so treated?

DR. BAEKELAND: Yes, nails can be driven in and screws can be used in the same way, with some precautions. Of course, the more Bakelite you put in the wood the harder it will become and the more resistance it will offer to screws or nails.

MR. HERING: I would like to ask what the coefficient of expansion and contraction is, compared to copper, because in coating copper coils in this way, the copper expands. Now, does that crack the coating or not?

DR. BAEKELAND: I have no accurate data to present; we are limiting ourselves in every instance to find out whether the results are good enough to start on a practical basis, and afterwards settle the other details. I cannot express to you in coefficients the rates of expansion, etc., but as I stated before, if you make a layer thin enough there is no trouble, and if you want to make the layer thicker, as in the case of chemical vessels, you simply introduce a filling material. But in the case of copper wire, where thin layers are used, there is no trouble resulting from irregular expansion.

MR. NORTHRUP: Mr. Chairman, I suppose each one here who is connected with manufacturing processes immediately begins to think of all the possibilities of this new substance for the processes in which he is interested. In our work we use perhaps $5,000 worth of hard rubber sheet a year, and, of course, I immediately think: Is it possible to use it as a substitute for hard rubber sheeting, which we now have to import from abroad because we cannot get the qualities we want in this country,—is it possible to use Bakelite, impregnating it with some kind of material, as a substitute for hard rubber sheeting, hard rubber rods and the many forms into which hard rubber is molded and used in the electrical industry? The requirements are, of course, that it shall have a high insulation efficiency, that it shall take a fine polish and be susceptible of drilling and being worked with machine tools. I should be very much obliged to Dr. Baekeland if he would answer that question.

DR. BAEKELAND: It is easy to answer that question, because it has been done. Without going into details, some of these applications are being utilized on a commercial scale since several months. In fact, I have waited before publishing anything about Bakelite until I was sure of at least some commercial applications being practicable.

Here is a pipe stem which is an excellent illustration of the utility of Bakelite B. The molding of this pipe stem was done

in a type-metal mold made in two halves. The mixture you see here, a cake of A with asbestos filling material, was put in the mold in a press and heated. The center wire formed the hole or channel in the stem. If the mass were transformed into C, the whole thing would probably split on account of contraction during polymerization; at least, if it did not split, you could never draw out the iron wire from the stem. The mass was simply heated two or three minutes, until it became Bakelite; then it was removed from the mold. While it was soft the wire was drawn out, and the pipe stem was then curved by giving it a turn or a twist, then put in cold water to solidify it.

If it was put in a Bakelizer, in this condition B, at high temperature, the stem would become elastic again and straighten itself. But in order to avoid that it was put into a box with some sand so as to keep its curved shape, and in this condition heated in the Bakelizer until it became C, and then it kept its shape permanently.

MR. A. H. COWLES: I would like to inquire if it would stand the action of concentrated or gaseous hydrochloric acid.

DR. BAEKELAND: Very well.

MR. COWLES: What is the density or specific gravity?

DR. BAEKELAND: The specific gravity of Bakelite C, made with a cresol, is about 1.25.

MR. E. S. LINCOLN: In using the material in connection with asbestos, what pressure is necessary to use in the molding?

DR. BAEKELAND: In the beginning we thought very high pressures were necessary. Then we found we could use very low pressures. The peculiarity which distinguishes Bakelite is the fact that it requires only moderate pressures, but high temperatures. The first application of heat melts A and gives the form. After that everything takes care of itself, and A becomes B and then C, which no longer melts. In the beginning, hydraulic pressures as high as 2,000 pounds to the square inch were used. Lately we have done very good molding with as low as 300, and even 200 pounds.

MR. LINCOLN: Is any advantage gained by increasing the pressure?

DR. BAEKELAND: Increased pressure is only necessary when an abundant quantity of filler is used, or if you use B exclusively. As soon as a mixture is made that flows easily, no further pressure is required. The principal requirement in the molding process is a temperature very high for such work, a temperature of 150° C. to 200° C.

PROF. S. A. TUCKER: I would like to ask Dr. Baekeland the probable comparative costs of finished Bakelite and viscose. Apparently viscose has gone out, due to the expense of its manufacture, but I should think that that was rather a cheap product.

DR. BAEKELAND: This is rather a commercial question, which it is hard to answer before a scientific body. I am amazed at the commercial instincts of dear Prof. Tucker. But I may say this, that it depends, of course, on the price at which A is sold, which is a matter that I am not prepared to present here in public. But I can state this, that the ultimate possibility is that Bakelite will ultimately be available at such a startlingly low price that a large number of applications will be possible, even beyond these I have mentioned.

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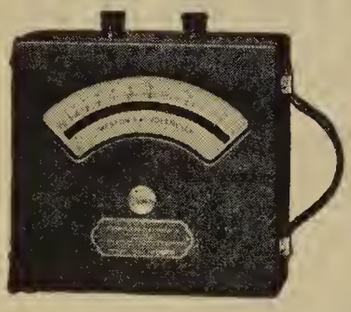

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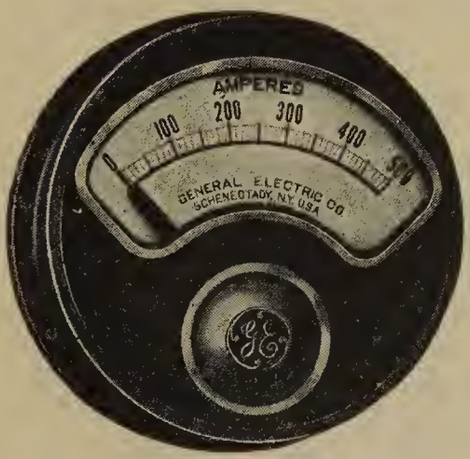

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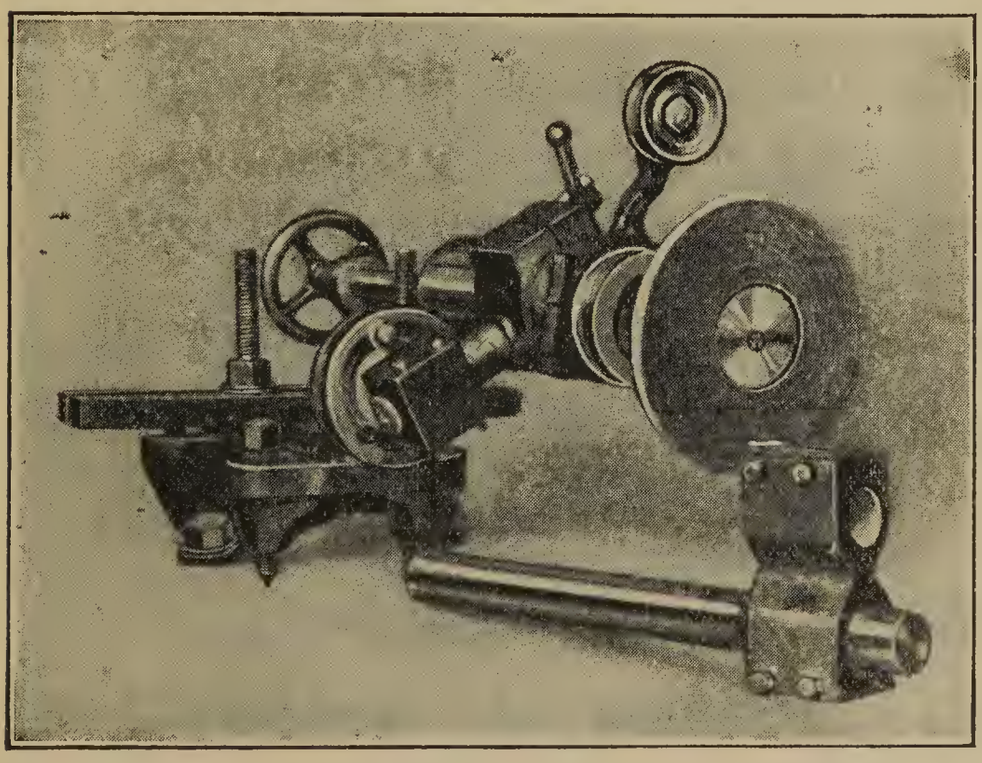

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